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University of Alberta

Unusual Low-Valent Binuclear Complexes of Rhodium Involving the Basic Bis(dimethylphosphino)methane Ligand

by

James Albert Jenkins ©

A thesis
submitted to the Faculty of Graduate Studies and Research
in partial fulfilment of the requirements
for the degree of Doctor of Philosophy

Department of Chemistry

Edmonton, Alberta
Spring, 1991

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C.P. Kubiak

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A.D. Hunter

K.R. Kopecky

S. Wanke

Date: February 7, 1991

To Vivian Jenkins and Albert Leithead

Abstract

The reaction of bis(dimethylphosphino)methane (dmpm) with $[RhCl(cod)]_2$ (cod= 1,5-cyclooctadiene) under CO yields the binuclear complex *trans*-$[RhCl(CO)(dmpm)]_2$ which was subsequently used to synthesize the species $[RhCl_2(CO)(dmpm)]_2$, *trans*-$[RhBr(CO)(dmpm)]_2$, $[Rh_2(CO)_2(\mu\text{-}Cl)(dmpm)_2][BF_4]$ and $[Rh_2(CO)_2(\mu\text{-}S)(dmpm)_2]$. The X-ray structure determination of $[RhCl_2(CO)(dmpm)]_2$ reveals a symmetrical complex with pseudo-octahedral metal centres. The chloro-bridged cationic species and its bromo analogue $[Rh_2(CO)_2(\mu\text{-}Br)(dmpm)_2][BF_4]$ (prepared from *trans*-$[RhBr(CO)(dmpm)]_2$ and $AgBF_4$) react reversibly with CO to produce the symmetrical tricarbonyl compounds $[Rh_2(CO)_2(\mu\text{-}X)(\mu\text{-}CO)(dmpm)_2][BF_4]$ (X= Cl, Br).

The reactions of *trans*-$[RhCl(CO)(dmpm)]_2$ and $[Rh_2(CO)_2(\mu\text{-}Cl)(dmpm)_2][BF_4]$ with the activated alkynes dimethyl acetylenedicarboxylate (DMAD) and hexafluoro-2-butyne (HFB) give products in which a single alkyne molecule bridges the two metal centres in a cis-dimetallated olefin fashion. Both neutral species react with $AgBF_4$ to provide the cationic species, $[Rh_2Cl(CO)_2(\mu\text{-alkyne})(dmpm)_2][BF_4]$ (alkyne= DMAD, HFB), respectively.

The heteroallene carbon disulfide (CS_2) reacts with *trans*-$[RhCl(CO)(dmpm)]_2$ and $[Rh_2(CO)_2(\mu\text{-}Cl)(dmpm)_2][BF_4]$ to yield the 2:1 adducts $[Rh_2Cl_2(CO)(C_2S_4)(dmpm)_2]$ and $[Rh_2Cl(CO)(C_2S_4)(dmpm)_2][BF_4]$ and ethoxycarbonyl isothiocyanate ($SCNCO_2Et$) reacts with *trans*-$[RhCl(CO)(dmpm)]_2$ to yield the 1:1 and 2:1 adducts $[Rh_2Cl_2(CO)\{\mu\text{-}SCNCO_2Et\}$-

(dmpm)$_2$] and [Rh$_2$Cl$_2$(CO)(μ-SCNC(S)N(CO$_2$Et)$_2$)(dmpm)$_2$].

The chemical reduction of *trans*-[RhCl(CO(dmpm)]$_2$ with NaOH under CO yields the highly fluxional species [Rh$_2$(CO)$_3$(dmpm)$_2$]. The reaction of this compound with CO and HBF$_4$•OEt$_2$ yielded the unstable, highly fluctional species [Rh(CO)(μ-CO)(dmpm)]$_2$, [Rh$_2$(CO)$_3$(μ-H)-(dmpm)$_2$][BF$_4$] and [Rh$_2$(CO)$_4$(μ-H)(dmpm)$_2$][BF$_4$].

The complexes [Rh$_2$(CO)$_2$(μ-DMAD)(dmpm)$_2$] and [Rh$_2$(CO)$_2$-(μ-HFB)(dmpm)$_2$] have been synthesized via the reduction of their dichloride precursors using sodium borohydride (NaBH$_4$) and lithium triethylborohydride (LiBEt$_3$H), respectively. The reaction of HBF$_4$•OEt$_2$ with these neutral alkyne products yields the unstable [Rh$_2$(CO)$_2$(μ-H)-(μ-DMAD)(dmpm)$_2$][BF$_4$] and the vinylic [Rh$_2$(CO)$_2$(F$_3$CC=C(H)CF$_3$)-(dmpm)$_2$][BF$_4$] complexes. The vinylic compound reacts immediately with CO to provide the unstable tetracarbonyl species [Rh$_2$(CO)$_3$(μ-CO)-(F$_3$CC=C(H)CF$_3$)(dmpm)$_2$][BF$_4$].

The series of bis(alkyne) complexes [Rh(CO)(μ-DMAD)(dmpm)]$_2$, [Rh$_2$(CO)$_2$(μ-DMAD)(μ-HFB)(dmpm)$_2$] and [Rh(CO)(μ-HFB)(dmpm)]$_2$ have been prepared and the X-ray structure determination of the latter two show that both alkyne ligands are coordinated in a cis-dimetallated fashion.

The mixed-metal complex [RhIrI$_2$(CO)$_2$(dppm)$_2$] (dppm= bis(diphenylphosphino)methane) was prepared and was found by solution spectroscopy to have an unsymmetrical sixteen-electron rhodium, eighteen-electron iridium configuration. Its reaction with AgBF$_4$ and CO provides the cationic species [RhIr(CO)$_2$(μ-I)(dppm)$_2$][BF$_4$] and

$[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][I]$, respectively. The reaction of $[RhIr(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]$ with DMAD results in the cis-dimetallated olefin complex $[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}DMAD)(dppm)_2][BF_4]$ which adds CO, yielding $[RhIrI(CO)_2(\mu\text{-}CO)(\mu\text{-}DMAD)(dppm)_2][BF_4]$.

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Well, it's a good thing this is almost over because I've about had it. To all those who come after me, *illegitimi noncarborundum*.

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List of Abbreviations and Symbols

anal.	analyses
C	celsius
ca.	circa (approximately)
calcd	calculated
cod	1,5-cyclooctadiene
cm	centimetres
d	doublet
dd	doublet of doublets
dt	doublet of triplets
dqr	doublet of quartets
dm	doublet of multiplets
ddt	doublet of doublet of triplets
DMAD	dimethyl acetylenedicarboxylate, $CH_3O_2C\text{-}C{\equiv}C\text{-}CO_2CH_3$
dmpm	bis(dimethylphosphino)methane, $(CH_3)_2PCH_2P(CH_3)_2$, also represented by . All dmpm ligands are bridging unless otherwise noted
dpam	bis(diphenylarsino)methane, $(C_6H_5)_2AsCH_2As(C_6H_5)_2$
dppm	bis(diphenylphosphino)methane, $(C_6H_5)_2PCH_2P(C_6H_5)_2$
dppe	1,2-bis(diphenylphosphino)ethane, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$
ETM	bis(ethylthio)methane, $(CH_3CH_2)SCH_2S(CH_2CH_3)$
EtOH	ethanol, CH_3CH_2OH
Et	ethyl, CH_3CH_2–

equiv	equivalent
h	hour(s)
HFB	hexafluoro-2-butyne, $F_3C-C\equiv C-CF_3$
IR	infrared
i-Pr	isopropyl, $-CH(CH_3)_2$
m	medium in IR, multiplet in NMR
M	molar
Me	methyl, CH_3-
MeOH	methanol, CH_3OH
mg	milligrams
min	minute(s)
mL	milliliters
μL	microliters
mm	millimetres
μmol	micromoles
mmol	millimoles
mol	mole
μs	microseconds
NMR	nuclear magnetic resonance
Ph	phenyl, C_6H_5-
ppm	parts per million
Py	pyridyl
q	quintet
qr	quartet
s	second(s), in tables; strong (IR), singlet (NMR)

sh	shoulder
sp	septet
t	triplet
tq	triplet of quintets
t-Bu	tertiary butyl, $-C(CH_3)_3$
THF	tetrahydrofuran, C_4H_8O
vs	very strong
w	weak
δ	chemical shift in NMR
η^{X}-	denotes X different donor atoms coordinated to the metal
Λ	molar conductivity
μ	denotes bridging ligands
ν	stretching mode in IR
Ω	ohms

Crystallographic Abbreviations and Symbols

a, b, c	lengths of the x, y, and z axes, respectively, of the unit cell
B	isotropic thermal parameter
deg (or °)	degrees
F_c	calculated structure factor
F_o	observed structure factor
h, k, l	Miller indices defining lattice planes, where the plane intersects the unit cell axes at $1/h$, $1/k$ and $1/l$ of the respective lengths of a, b and c
p	experimental instability factor (used in the calculation of $\sigma(I)$ to downweight intense reflections)
R	residual index (a measure of agreement between calculated and observed structure factors)
R_w	weighted residual index
V	unit cell volume
w	weighting factor applied to structure factor
Å	Angstrom(s) (1 Å = 10^{-10} meters)
α, β, γ	angles between b and c, a and c, and a and b axes, respectively, of unit cell
β_{ij}	anisotropic displacement parameters
λ	wavelength
ρ	density
σ	standard deviation

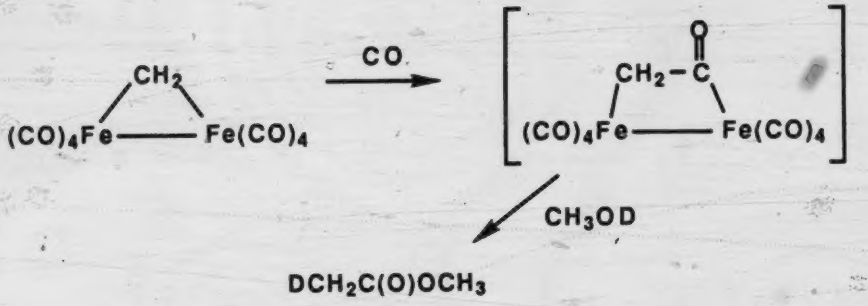
Chapter 1

Introduction

General Introduction.

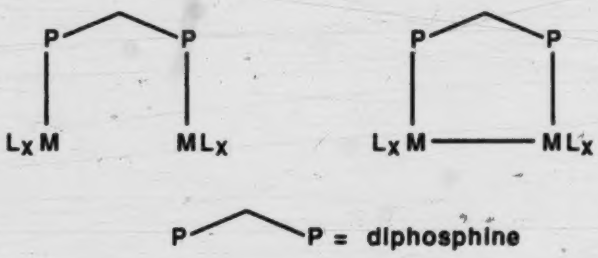
The synthesis of organic molecules using the mild reaction conditions of homogeneous catalytic systems has, for some time, been an attraction to industry as a means of cutting costs of production.[1,2a] The good selectivity of homogeneous systems is also expected to be of greater significance as more emphasis is placed on the production of high purity, complex organic molecules such as pharmaceuticals.[1] The role that transition metal complexes may play in these organic transformations is of considerable interest to organometallic chemists. Much of this interest has recently focused on the cooperative use of adjacent metal centres in multinuclear, organometallic compounds to activate organic molecules and provide new patterns of reactivity and modes of coordination which are not observed for mononuclear complexes.[3-8] Ultimately such new reactivity might have applications in both homogeneous and heterogeneous catalytic processes.

Bimetallic organometallic clusters may also prove effective for modeling the reactions which take place at the bulk-solid metal surfaces in heterogeneous systems.[2b,3,4,9a] Many heterogeneous processes such as the Fischer-Tropsch formation of linear hydrocarbons, olefins and alcohols from CO and H_2 appear to involve more than one reactive metal site but the actual mechanisms are still not fully understood.[2a,2b,9a] Having more than one metal centre in the model complex may provide a better representation of a portion of the bulk surface than a mononuclear species could. The isolation and subsequent characterization of multinuclear compounds which represent intermediates in the heterogeneous system might help to establish a link to the well known chemistry of mononuclear homogeneous systems. By this means a thorough understanding of heterogeneous reaction mechanisms may possibly be realized. Some success in this area has already been achieved[3,9a] as shown by the example illustrated below. This model reaction has relevance to the way in which oxygenated products are formed in the Fischer-Tropsch process via a proposed bridged ketene intermediate.[10]



Binuclear complexes represent the prototype for clusters, being the simplest system in which metal-metal cooperativity effects can be observed. Historically, the majority of binuclear systems studied has involved those in which both metals are the same. Recently, however, heterobinuclear systems have received an increasing amount of attention as a means of studying the complementary effects of two metal centres with different chemical properties in the same complex.[6,8,11-14] In addition to the potential for new reactivity patterns which are substantially different from those of homobinuclear complexes, the investigation of these types of compounds might also be instrumental in determining the reaction mechanisms of heterogeneous catalyst combinations consisting of two metallic elements.

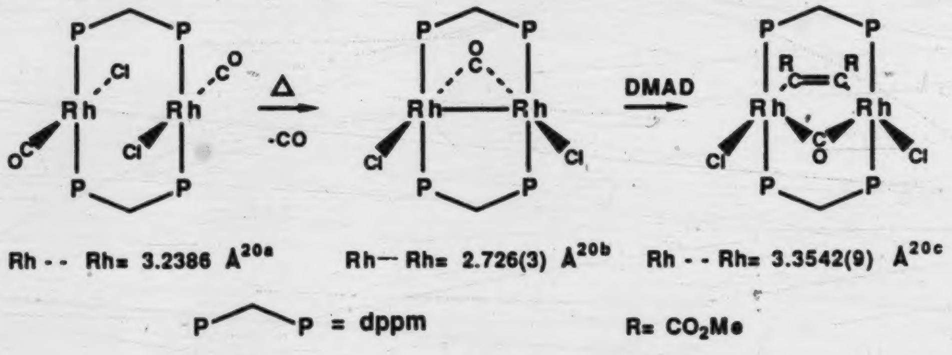
A primary concern in the reaction of binuclear complexes with organic substrates is that the compound of interest may fragment into mononuclear components under the reaction conditions. The series of diphosphine ligands of the form, $R_2P(CH_2)_nPR_2$ (R= alkyl, alkoxide, aryl), are quite versatile in this regard, being able to bind to two separate metal centres in a bridging fashion through strong metal-phosphorus bonds.[5,6,15,16] Those which are best suited for a bridging role have n= 1 since the inherent strain of a four-membered ring, encountered when the diphosphine is chelated to one metal, is at a maximum.[4,5,17] This is exemplified by the rhodium complex *trans*-[RhHCl(η^2-dppm)$_2$][BPh$_4$] [18] (dppm= bis(diphenylphosphino)methane, n= 1) which contains a chelated dppm P-C-P angle of ca. 96°, much less than the ideal 109.5° angle for a tetrahedral sp^3 carbon atom. Thus ligands such as dppm often coordinate in a monodentate fashion or form a five-membered "open" or closed ring (depending on whether or not a metal-metal bond is present)



with two metal centres.[5,6] In contrast, dppe (bis(diphenylphosphino)-

ethane, ~~n= 2)~~ requires only one additional atom to complete a relatively unstrained five-membered ring and subsequently shows a greater propensity for chelation to a single metal centre.[5] When the length of the carbon chain in the diphosphine ligand is greater than two, steric problems result and the tendency for chelation drops again. This aids in the formation of dimers and polymers but the metal atoms are quite often held too far apart to be of use in the study of their combined interaction with organic substrates.

The "short bite" and the flexibility of the P-C-P angle of the diphosphine ligand (n= 1) allows for the bridge coordination of a variety of different size molecules between the two metals without the fragmentation of the complex.[19] This is important since many reactions are of the insertion type, involving the making or breaking of a metal-metal bond, a process which is accompanied by a change in the metal-metal separation, as shown in the following reaction sequence.[20]



The diphosphine ligand most commonly used for holding two metal centres together has been dppm. Several extensive reviews documenting the chemistry of complexes containing this ligand have appeared and it has generally become the standard by which other related diphosphine ligands are measured.[5,6] One, two, and in a few cases, three dppm molecules have been successfully incorporated into the skeletal framework of binuclear complexes but two is the most common among Group VIII metal species. Several diphosphine analogues of dppm containing different phosphorus substituents (R= Me, Et, *i*-Pr, *t*-Bu) have been utilized to a lesser extent in the synthesis of binuclear complexes.[5,6,21-24] These ligands also possess a short-bite and exhibit a preference for bridge coordination. Like the well documented mononuclear complexes containing tertiary phosphine ligands,[25] it has become evident that varying the R groups of the diphosphine allows one to adjust its steric and electronic properties and thereby change the reactivity of the metal centres to which it is attached. At the time this work was initiated only a limited number of studies of binuclear complexes containing these alternate diphosphines had been undertaken and the potential differences in reactivity they might produce had yet to be fully realized. Thus an investigation was undertaken into the preparation and reactions of dmpm-bridged dirhodium complexes (dmpm= bis(dimethylphosphino)methane), the results of which are contained in this thesis (Chapters 2-5). Of particular interest to us were the changes in reactivity that might occur upon substitution of dmpm for dppm in binuclear complexes and how these changes might affect the coordination of organic substrates. The choice of the dirhodium system was made on the basis of the wealth of known "$Rh_2(dppm)_2$" chemistry [5,6] which could be drawn upon for comparison purposes in evaluating the reactivity of the

"$Rh_2(dmpm)_2$" system. In addition, studies on mixed-metal "$RhIr(dppm)_2$" complexes have been carried out (Chapter 6) as a means of gaining some insight into the reactivity of heterobinuclear complexes.

The remainder of this introduction is divided into three sections. The first deals with a general discussion of the steric and electronic properties of dmpm and how they relate to those of dppm in terms of the formation of binuclear complexes. This is followed by a review of dmpm complexes with a focus on the types of structures and reactivities which have been observed. Since this study was primarily concerned with binuclear complexes, a discussion of dmpm species with a nuclearity greater than two has been excluded. Finally, the objectives of this investigation are presented.

General Properties of Dmpm

The dmpm ligand itself was first prepared by Karsch and Schmidbaur [26] from the reaction of $(CH_3)_2PCl$ with Li_2CH_2 or $LiCH_2P(CH_3)_2$. It is the simplest possible bis(tertiaryalkylphosphine) and being extremely pyrophoric is much more difficult to handle than dppm. This characteristic may account for part of the reason why it has been utilized to a lesser extent in the preparation of transition metal complexes. However, it offers significant advantages over dppm as a bridging ligand in possessing a relatively small steric bulk and presumably a stronger σ-donating ability.[21,22,24a,24e,27-32] Both of these factors result in an apparent enhancement in reactivity of dmpm complexes as compared to their dppm analogues.[24a,31b,31c] The relative size of the two ligands is most easily realized upon comparison of their cone angle values (dppm, 121°; dmpm, 103°).[25,33] The term cone angle was developed by Tolman who defined it as the apex angle of a cone which is centred on the metal and encloses the van der Waals radii of the outermost atoms of the phosphine substituents.[25] This method of size measurement has since been found to suffer from inaccuracies but it remains in common use and works well for illustrating the steric differences of a series of similar ligands.[34,35]

The size of the substituents on phosphorus is an important consideration in terms of the type of diphosphine coordination and the effect on the reactivity of the metal centres involved. Those ligands containing bulkier substituents such as phenyl groups will be more apt to form a chelated species with a strained four-membered ring.[5,24,36] We look to dppm as an example and note that although there is a tendency for this ligand to form bridged species there are also many chelated examples as well.[5,6] By comparison, dmpm, which contains the much smaller methyl substituents, proportionally shows a much greater tendency to form bridged species than dppm. Puddephatt and coworkers have carried out a number of studies on platinum-diphosphine complexes and have shown that increasing the steric bulk of the diphosphine substituents favours chelate formation and decreases the reactivity of the compound towards oxidative addition.[24,36] In particular, for the system $[Pt(CH_3)_2$-(diphosphine)$]_x$ (x= 1) the chelated monomeric form is more stable when the diphosphine is dppm while the dimeric form predominates when the diphosphine is dmpm (x= 2).[24b] Hence, the size of the substituents appears to play an important role in the nuclearity of the complexes.[16,24b]

The sterically undemanding dmpm ligand should also enhance the reactivity of bimetallic complexes relative to their dppm analogues by allowing easier access to the metal centres. Again Puddephatt has found that the dppm derivative of $[Pt(Me)_2(diphosphine)]_2$ does not react with ICH_3 whereas the dmpm derivative does, the difference in behavior being attributed somewhat to the large size of the phenyl substituents of dppm.[24a,37]

Electronically, dmpm is commonly considered to be more basic than dppm.[21,22,29-31] Although it is not specifically stated, this assumption apparently relies on organic substituent effects in which an alkyl group is expected to be more electron-donating than an aryl group.[38] Evidence to support this assumption can be found in several investigations into the relative basicities of tertiary phosphines.[25,39-43] One of the more widely quoted studies by Tolman uses the A_1 carbonyl stretching frequency of $[Ni(CO)_3(PR_3)]$ complexes to derive substituent electronic parameters, χ_i, ($\chi_i(Me)= 2.6\ cm^{-1}$, $\chi_i(Ph)= 4.3\ cm^{-1}$) the outcome of which is a relative basicity ordering of $PMe_3 > PMe_2Ph > PMePh_2 > PPh_3$ for related monodentate phosphines.[25,40] The same ordering has been established by a variety of means including pK_a measurements [39] and enthalpies of protonation.[43] It should be noted however that gas-phase studies (including proton affinity measurements) on tertiary phosphines [44] and diphosphines [45] indicate the reverse order to be correct. It has been suggested that this apparent inconsistency may be explained in terms of domination of the chemical reactivity of the phosphines by the differences in steric effects such as solvation energies between phenyl and methyl derivatives when in solution. Most recently, Giering and coworkers have evaluated several methods of basicity measurements in their efforts to classify phosphorus(III) ligands as either predominantly σ-donor or σ-donor/π-acceptor ligands.[46] These studies indicate that in solution at least, χ_i and pK_a values do represent reasonable measures of the σ-donicity of σ-donor phosphines such as PMe_3 and PPh_3. Therefore, by analogy, it can be stated with assurance that in solution dmpm is more basic than dppm.

Given the σ-donating ability of dmpm, its incorporation into a transition metal complex would be expected to increase the electron-density at the metal centres, thereby enhancing the reactivity of the compound towards oxidative addition. Since the metal atoms are often already in low oxidation states (0, I, II) it is necessary to have π-acid ligands such as CO present in order to alleviate the build-up of electron-density and stabilize the complex. The frequencies of the resulting carbonyl stretching vibrations in the infrared spectrum can be used as a measure of the electron density at the metal, the reasoning being that a more electron-rich complex will result in an increase in the amount of metal-to-carbonyl d_π-p_π^* backbonding. This in turn weakens the C-O bonding interaction and produces a lower frequency CO stretch.[2c, 9b] In this respect the dmpm analogues of dppm compounds generally show a decrease in ν(CO) of up to 12 cm^{-1}.[15a,21,47,48]

Review of Dmpm Complexes

Prior to 1985, at the time this work was begun, the number of dmpm complexes reported in the literature was quite limited.[15a,21,22a,24a,24d,47a,49-51] Although dmpm tends to form bridging complexes, many of the first investigations resulted in the formation of chelated dmpm compounds.[21,22a,24e,24g,33,49,52-54] Karsch prepared several series of mononuclear iron, cobalt and nickel species of the form $[M(PMe_3)_3(\eta^2\text{-dmpm})]$ [49a,49b] and $[M(PMe_3)(\eta^2\text{-dmpm})_2]$ (M= Fe, Co^+, Ni^{+2})[22a] and related species.[49c,49d] Interestingly, the cobalt species $[Co(PMe_3)(\eta^2\text{-dmpm})_2][Cl]$ readily converts to the dimer $[Co_2(PMe_3)_2\text{-}(\mu\text{-}PMe_2)(dmpm)_2][Cl]$ upon warming in solution.[22] The series of similar mononuclear Group VI complexes $[M(CO)_4(\eta^2\text{-dmpm})]$ (Cr, Mo, W) were also synthesized by the research group of King from the replacement of norbornadiene (NBD) in $[M(CO)_4(NBD)]$.[21] Wilkinson [52a] and Karsch [33] independently reported the incorporation of three dmpm ligands onto one metal centre in the synthesis of $[Fe(\eta^1\text{-dmpm})(\eta^2\text{-dmpm})_2]$ and Puddephatt and coworkers prepared the platinum species $[PtI_2(\eta^2\text{-dmpm})]$[24g] and $[PtIMe_3(\eta^2\text{-dmpm})]$.[24e] With a single exception ($[(\eta^5:\eta^5\text{-fulvalene})Mo_2(CO)_5(\eta^2\text{-dmpm})]$),[54] these mononuclear species represent the only examples in which dmpm is chelated and it seems appropriate to attribute this small number of such species to the preference of dmpm for bridge coordination. This certainly appears to be true in light of the studies carried out by Puddephatt on platinum complexes in which several mononuclear chelated-dppm complexes were successfully isolated but very few such dmpm complexes were obtained.[24] We note, however, that it is not clear whether this trend is related to the chemistry and it truly reflects the nature of the phosphine or whether early studies were biased towards the synthesis of chelated species and in recent years most studies have been concerned with the synthesis of higher nuclearity species.[6,28a,55]

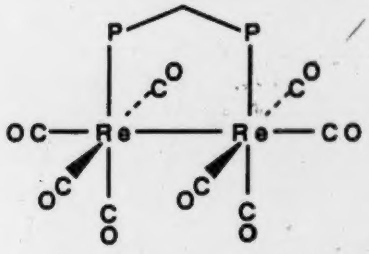
Mononuclear complexes containing one,[33,50,52,56] two [36] or three [21] monodentate dmpm ligands have been prepared. One potential value of mononuclear chelated-dmpm and monodentate-dmpm compounds lies in their ability to function as precursors for the synthesis of homo- and heterobimetallic complexes. This can take place directly by coordination of a second metal centre to the free end of a η^1-dmpm ligand or indirectly via a ring opening reaction followed by η^1-dmpm coordination. The research group of Shaw has made extensive use of these methods to prepare a wide variety of platinum and palladium complexes from the reaction of starting materials such as $[Pt(CCR)_2(\eta^1\text{-dppm})_2]$ [57] and $[Ir(CO)(\eta^2\text{-dppm})_2][Cl]$ [58] with the appropriate metal complex. Puddephatt has recently developed a similar method for synthesizing unsymmetrical "$Pt_2(dmpm)_2$" complexes such as cis, cis-$[Ph_2Pt(\mu\text{-dmpm})_2PtMe_2]$ and cis, trans-$[Ph_2Pt(\mu\text{-dmpm})_2Pt\text{-}ClR]$ (R=Me, Ph) using the mononuclear species cis-$[PtPh_2(\eta^1\text{-dmpm})_2]$, (reaction 1.1).[36] In general, the use of mononuclear-dmpm species (with

$$[PtPh_2(\eta^1\text{-dmpm})_2] \; + \; 1/2[Pt_2Me_4(\mu\text{-SMe}_2)_2] \longrightarrow \text{cis, cis-}[Ph_2Pt(dmpm)_2PtMe_2] \qquad 1.1$$

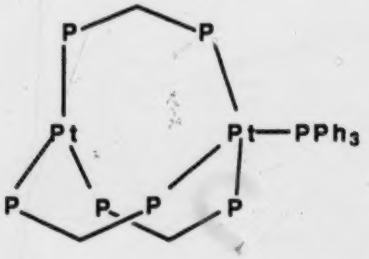
either monodentate or chelated dmpm) for the preparation of binuclear-dmpm complexes, is not widespread. We are aware of only one other report in which a binuclear, dmpm-bridged compound has been prepared from a mononuclear dmpm-species (reaction 1.2).[52b]

$$[Fe(\eta^1\text{-dmpm})(\eta^2\text{-dmpm})_2] \xrightarrow[Cr(CO)_6]{h\nu} [FeCr(CO)_6(dmpm)_2] \qquad 1.2$$

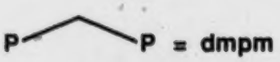
Binuclear dmpm complexes have been synthesized directly from the reaction of dmpm with mononuclear[22,32,36,56,59-64] and even trinuclear[48] transition metal compounds but the majority have resulted from the reaction of dmpm with a preformed dimer such as $[Pt_2(Me)_4(\mu\text{-}SMe_2)_2]$,[24b] $[Re_2Cl_8(n\text{-}Bu_4N)]$[65] or $[MCl(cod)]_2$ (M= Rh, Ir).[62,66] One,[15a,21,23,28,47,67-69] two,[15a,16,21-24,28b,29-32,36,47b,51,52b,56,61-64,66,70-73] and in a few instances, three[21,23,56,59,60,65,74] dmpm ligands have been incorporated into the products in a bridging manner. Representative examples of these species are illustrated below. All structural types shown have been observed in related "$M_2(dppm)_X$" chemistry.[5,6]



A

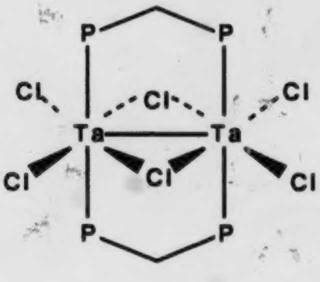


B

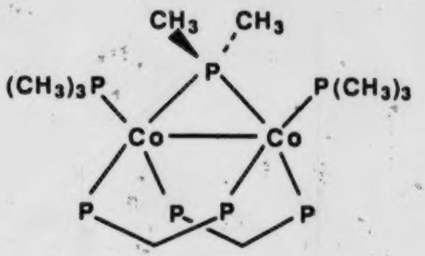


Several studies involving complexes of type **A** have shown one dmpm ligand (as well as other similar diphosphines) to be effective in the stabilization of the binuclear molecule towards dissociation relative to their non-diphosphine containing analogues.[47a] Examples of "$M_2(dmpm)_3$" compounds (type **B**[59]) have been reported.[21,23,56,59,60,65,74] but their subsequent chemistry is limited and for the most part they appear to be a structural curiosity.

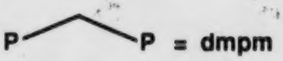
The bulk of binuclear-dmpm complexes contain two ligands which are coordinated either in a trans, trans fashion as in C[70b] or a cis, cis fashion as in D,[22] both of which are commonly observed. The trans, trans diphosphine geometry shown for $[Ta_2Cl_6(dmpm)_2]$ (C)[70b] has an edge-sharing bi-octahedron geometry and represents only one of the possible trans, trans diphosphine arrangements. Cotton et al. have structurally characterized a series of Group V, VI and VIII chloride complexes, $[M_2Cl_4(\mu\text{-}Cl)_2(dmpm)_2]$ (M= Ta, Nb, Cr, Ru),[70a,b,f] $[Mo_2Cl_4(dmpm)_2]$[29] and $[V(\eta^2\text{-}BH_4)(\mu\text{-}Cl)(dmpm)]_2$[70a] all of which have the geometry illustrated for C. In general the chloride species listed above closely resemble their direct dppm analogues or related $[M_2Cl_X(dppm)_2]$ (X= 4,6) complexes. One major difference of note concerns the niobium-hexachloride compound[70a] in which the dmpm counterpart possesses the bridging diphosphine structure of C yet the dppm analogue[75] has a chelated diphosphine structure with two chloride bridging ligands. Other forms of trans, trans geometry include the face-to-face, bi-square planar



C



D



arrangement of *trans*-$[PtIMe(dmpm)]_2$,[32] the metal-metal bonded square planar $[PdBr(dmpm)]_2$ [31b] as well as the singly bridged A-frame structures of $[Ir_2(\mu\text{-}CH_2)(CO)_4(dmpm)_2][CF_3SO_3]_2$ [73d] and $[Pd_2Cl_2(\mu\text{-}CO)(dmpm)_2]$.[31c,51a]

Complexes such as $[Co_2(PMe_3)_2(\mu\text{-}PMe_2)(dmpm)_2]$ (**D**),[22] possessing the cis, cis-diphosphine geometry, are alternatively described as binuclear W-frame or cradle compounds. Interestingly, most compounds exhibiting this type of geometry have Group VIII metal centres.[16,22,24,31a,31c,36,54,61,70e,71,73c] A cis, trans arrangement of dmpm ligands has been observed for several binuclear complexes such as $[Ph_2Pt(dmpm)_2PtClR]$ (R=Me, Ph),[36] the manganese species $[Mn_2(CO)_6(dmpm)_2]$ [73a] and most recently for $[Ir_2(CO)_3(dmpm)_2]$.[73e]

Group VIII "$M_2(dmpm)_2$" compounds exhibit both the cis, cis and trans, trans diphosphine geometry of **C** and **D** and have been the most extensively studied dmpm complexes with respect to the variety of organic molecules which can be coordinated between the two metal centres.[24d,24e,24f,31c,31d,36,51,62,66,73c,73d,73e] Many of these investigations have focused on the dmpm analogues of "$M_2(dppm)_2$" systems and the differences in structure and reactivity that have been brought about by substitution of the diphosphine ligand. For example, Puddephatt's work on "$Pt_2(diphosphine)_2$" complexes (discussed earlier) [24] has shown that decreasing the bulk of the phosphorus substituents favours bridge formation and increases the reactivity of the binuclear compounds towards oxidative addition. Gladfelter has recently synthesized the species $[Ru_2(CO)_4(\mu\text{-}CO)(dmpm)_2]$ and found it to be highly reactive towards protonation and the substitution of alkynes for carbon monoxide.[48] This complex is structurally similar to the diphosphine analogues $[Ru_2(CO)_4(\mu\text{-}CO)(dppm)_2]$ [72,76] and $[Ru_2(CO)_4(\mu\text{-}CO)\{(MeO)_2PN(Et)P(OMe)_2\}_2]$,[15a] but is presumably more electron rich, as evidenced by the lower energy carbonyl stretching vibrations in it's infrared spectrum ($\nu(CO)$ is 10 cm^{-1} lower than that of the direct dppm analogue).

A third example involves the insertion of a variety of electrophilic molecules (CO, CNMe, SO_2, CS_2) into the M-M bond of $[Pd_2Cl_2(dmpm)_2]$ [31c] to provide products which are similar in most respects to the palladium and platinum dppm counterparts.[5,6] However, there is an apparent greater stability of the "$Pd_2(dmpm)_2$" analogues which was suggested to be a result of the increased donor ability of dmpm over dppm.[31c] Significantly, and in contrast to the corresponding dppm species, $[PdCl(dmpm)]_2$ was found to be both soluble and stable in aqueous solution.[31b,51a] This behavior led to the discovery that substitution of hydroxide for chloride to yield $[Pd(OH)(dmpm)]_2$, also occurred. The subsequent insertion of CO into the metal-metal bond of the dihydroxide species has been included as a part of a proposed mechanism for the homogeneous catalysis of the water-gas-shift reaction.[51b]

Kubiak and coworkers have taken advantage of the steric and electronic properties of dmpm to synthesize several highly reactive "$Ir_2(dmpm)_2$" carbonyl and isocyanide complexes.[31a,31d,62,73c,73e] The complex $[Ir_2(CO)_3(dmpm)_2]$ reacts with liquid CO_2 under pressure to provide the tetracarbonyl $[Ir(CO)_2(dmpm)]_2$ and an interesting carbonate species $[Ir_2(CO)_2(\mu\text{-}CO_3)(dmpm)_2]$.[73e] The cradle compound $[Ir(CNR)(\mu\text{-}CNR)(dmpm)]_2$ reacts with Al_2Et_6 in a carbon-carbon bond forming reaction to yield $[Ir_2(CNR)_2\{C_2(NR)_2AlEt_2\}(dmpm)_2]$ [31a] (R= 2,6-$Me_2C_6H_3$) in which two isocyanide ligands are coupled to each other and both are condensed with the $AlEt_2$ fragment.

Objectives of this thesis

The work presented in this thesis was carried out in an attempt to widen the scope of binuclear diphosphine complexes and gain a better understanding of the reactivity which is possible when two metal centres are held in close proximity in the same molecule. The majority of these investigations have been concerned with "$Rh_2(dmpm)_2$" chemistry. In addition, limited studies of mixed-metal "$RhIr(dppm)_2$" complexes have also been carried out.

At the time this work was initiated no "$Rh_2(dmpm)_2$" compounds had been reported in the literature. The development of this chemistry was broken down into the following steps:

1. The design of a convenient procedure for the preparation of a "$Rh_2(dmpm)_2$" complex which could be used as a precursor for the synthesis of other such species. Given the tendency of dmpm to form bridging complexes, efforts were focused on the utilization of preformed dimers such as $[RhCl(cod)]_2$ and $[RhCl(CO)_2]_2$ to prepare "$Rh_2(dppm)_2$" complexes.
2. The preparation and characterization of a number of "$Rh_2(dmpm)_2$" analogues of known "$Rh_2(dppm)_2$" and "$Ir_2(dppm)_2$" complexes, in order to determine the effects on reactivity that the smaller and presumably more basic (relative

to dppm) dmpm ligand would have on the reactivity of these binuclear species.

3. The preparation and study of reduced Rh(0) binuclear dmpm species. It was anticipated that such products would be highly susceptible to oxidative addition reactions of organic substrates.

A limited investigation into mixed metal "RhIr(dppm)$_2$" chemistry was undertaken as a means of obtaining related species which would be useful for comparison purposes to evaluate the reactivity of "Rh$_2$(dmpm)$_2$" complexes.

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Chapter 2

Binuclear Bis(dimethylphosphino)methane Complexes of Rhodium and Some Comparisons with the Bis(diphenylphosphino)methane Analogues of Rhodium and Iridium*

Introduction

Although the diphosphine bis(diphenylphosphino)methane (dppm) has been used extensively as a bridging ligand in the preparation of binuclear complexes,[1,2] the steric bulk of the large phenyl rings may inhibit the accessibility of substrate molecules to the metal centres. The diphosphine bis(dimethylphosphino)methane (dmpm) is also a good bridging ligand [2] and offers a partial solution to the steric problem by virtue of the methyl groups which are less sterically demanding than phenyl substituents. (The cone angles of dppm and dmpm are 121° and 103°, respectively.[3,4] See Chapter 1 for a discussion on the relative steric bulk of these two ligands.) In addition, the presumed greater basicity of dmpm [5,6] should increase the nucleophilicity of the metals. It has been anticipated that both of these features should lead to an even richer chemistry of binuclear-dmpm complexes than that demonstrated for binuclear-dppm species. For these reasons, several groups have investigated the synthesis of such compounds.[7-11]

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This chapter describes the preparation and characterization of a series of binuclear dmpm-bridged complexes of rhodium. The results of this investigation are compared with the chemistry of reported binuclear dppm-bridged complexes of rhodium [12-17] and iridium [18,19] in order to determine the effect on reactivity that substitution of the the dmpm ligand has on the binuclear species.

Experimental Section

General Comments. All solvents were appropriately dried and degassed prior to use under an atmosphere of dinitrogen (see Appendix I). Reactions were routinely carried out under Schlenk conditions using prepurified dinitrogen which had been passed through columns containing Ridox and 4A molecular sieves in order to remove traces of oxygen and water. Bis(dimethylphosphino)methane (dmpm) and bis(diphenylphosphino)methane (dppm) were purchased from Strem Chemicals, hydrated rhodium trichloride was purchased from Johnson-Matthey, dimethyl acetylenedicarboxylate (DMAD), 1,5-cyclooctadiene (cod), thionyl chloride ($SOCl_2$) and silver tetrafluoroborate ($AgBF_4$) from The Aldrich Chemical Company, and sodium sulfide hydrate ($Na_2S \cdot 9H_2O$) from The J. T. Baker Chemical Company. Carbon monoxide (C. P. grade) and high purity chlorine were purchased from Matheson, ^{13}CO (99%) from Isotec Inc. and hexafluoro-2-butyne (HFB) from SCM, PCR Incorporated. These and all other reagent grade chemicals were used as received. $[RhCl(cod)]_2$ [20] and *trans*-$[RhCl(CO)(dppm)]_2$ [13] were prepared by the reported procedures. The compound $[Rh_2(CO)_2(\mu\text{-}Cl)(dppm)_2]^+$ was prepared as the $[BF_4]^-$ salt by the addition of one equiv of $AgBF_4$ to a THF slurry of *trans*-$[RhCl(CO)(dppm)]_2$. After reaction (1 h) the solvent was removed under vacuum and the subsequent workup was carried out in dichloromethane solution.

Infrared spectra were recorded on a Nicolet 7199 spectrometer with the use of Nujol mulls on KBr plates or in solution (CH_2Cl_2, THF) in NaCl cells. The ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker WH-200 and AM-400 instruments. The ^1H NMR spectra were recorded at 200 MHz or 400 MHz, the $^{13}C\{^1H\}$ NMR spectra at 100 MHz and the $^{31}P\{^1H\}$ NMR spectra at 81 MHz or 161 MHz. Phosphorus chemical shifts were measured relative to 85% phosphoric acid. An internal deuterium lock (usually CD_2Cl_2, $(CD_3)_2CO$ or C_4D_8O) was used for all samples. For all nuclei, positive chemical shifts are downfield from the standards.

Elemental analyses were performed within the department. Conductivity measurements were made using a Yellow Springs Instrument Model 31 conductivity bridge using approximately 1 X 10^{-3} M solutions in dichloromethane or nitromethane. All compounds which were isolated in solid form were found to react with air over a period of several hours so appropriate precautions were taken for their storage and handling.

Preparation of Compounds. (a) *trans*-$[RhCl(CO)(dmpm)]_2$ (1). The compound $[RhCl(cod)]_2$ (500 mg, 1.02 mmol), dissolved in acetone (50 mL) to which approximately 0.25 mL of water had been added, was refluxed under an atmosphere of carbon monoxide for 10 min. A solution of dmpm (315 μL, 2.03 mmol) in acetone (10 mL) was added via syringe over a period of 5 min. Refluxing under a carbon monoxide atmosphere was continued for a further 5 min. The solution was then cooled and the solvent was removed by cannula under positive N_2 pressure. The red-orange solid was washed repeatedly with diethyl ether, dried in vacuo, and collected in 90% yield (552 mg). Anal. Calcd for $C_{12}Cl_2H_{28}O_2P_4Rh_2$: C, 23.8%; Cl, 11.7%; H, 4.6%. Found: C, 23.8%; Cl, 11.7%; H, 4.7%.

(b) *trans*-[RhBr(CO)(dmpm)]$_2$ (2). The compound *trans*-[RhCl(CO)-(dmpm)]$_2$ (1) (250 mg, 0.413 mmol) and NaBr (425 mg, 4.13 mmol) were placed in a Schlenk tube under a dinitrogen atmosphere. A solvent mixture of CH_2Cl_2 (15 mL) and CH_3OH (10 mL) was added and the orange slurry stirred for 16 h. The solvents were removed under vacuum, CH_2Cl_2 (35 mL) was added, the mixture was stirred for 10 min, and the solution filtered through Celite. The volume of this solution was reduced to ca. 10 mL under a stream of dinitrogen, diethyl ether (35 mL) was added, the solution cooled to 0°C and the solvents removed by cannula under positive N_2 pressure. The orange powder was washed with small portions of THF (10 mL), dried under a stream of dinitrogen and collected in 65% yield (187 mg). This compound proved to be a nonelectrolyte in THF ($\Lambda(10^{-3}$ M$) = 0.8\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$). Anal. Calcd for $Br_2C_{12}H_{28}O_2P_4Rh_2$: Br, 23.0%; C, 20.8%; H, 4.1%. Found: Br, 23.1%; C, 21.2%; H, 4.2%.

(c) [RhCl$_2$(CO)(dmpm)]$_2$ (3). To a solution of *trans*-[RhCl(CO)-(dmpm)]$_2$ (1) (100 mg, 0.165 mmol) in CH_2Cl_2 (10 mL) was added 1 equiv of $SOCl_2$ (14.0 µL, 0.165 mmol). Upon addition, the clear red-orange solution immediately turned dark and then gradually lightened to red with the precipitation of an orange solid. Stirring was continued for 20 min, after which diethyl ether (20 mL) was added to ensure complete precipitation of the solid. The solvents were removed by cannula under positive N_2 pressure, the solid washed with diethyl ether, dried under a stream of dinitrogen and collected in 92% yield (103 mg) as an brown-orange powder. Anal. Calcd for $C_{12}Cl_4H_{28}O_2P_4Rh_2$: C, 21.3%; Cl, 21.0%; H, 4.2%. Found: C, 21.2%; Cl, 20.9%; H, 4.0%.

(d) [$Rh_2(CO)_2(\mu$-Cl)(dmpm)$_2$][BF_4] (4). To a slurry of *trans*-[RhCl(CO)-(dmpm)]$_2$ (**1**) (100 mg, 0.165 mmol) in THF (15 mL) was added a solution of $AgBF_4$ (32.2 mg, 0.165 mmol) dissolved in THF (10 mL). After stirring for 40 min the solvent was removed under vacuum and the product redissolved in CH_2Cl_2 (8 mL). Silver chloride was removed by filtration of the solution through a pad of Celite. The reactions of **4** were carried out on the amber coloured filtrate solution based on 100% conversion of complex **1**. Compound **4** could be obtained in solid form by reduction of the filtrate volume under a stream of dinitrogen followed by addition of diethyl ether but it was found to react quickly with traces of air. Compound **4** was determined to be a 1:1 electrolyte in nitromethane solutions ($\Lambda(10^{-3}$ M$)=75$ Ω^{-1} cm^2 mol^{-1}).

(e) [$Rh_2(CO)_2(\mu$-Br)(dmpm)$_2$][BF_4] (5). To a slurry of *trans*-[RhBr(CO)-(dmpm)]$_2$ (**2**) (100 mg, 0.144 mmol) in THF (10 mL) was added a solution of $AgBF_4$ (28.1 mg, 0.144 mmol) dissolved in THF (10 mL). After stirring the solution for 1 h the solvent was removed under vacuum and the product redissolved in CH_2Cl_2 (20 mL). Silver bromide was removed by filtering the dark orange solution through a pad of Celite. The further reactions of compound **5** were carried out on the amber coloured filtrate solution based on 100% conversion of complex **2**. Compound **5** could be obtained in solid form by reduction of the filtrate volume under a stream of dinitrogen followed by addition of diethyl ether, but it was found to react quickly with traces of air. Compound **5** was determined to be a 1:1 electrolyte in CH_2Cl_2 solution ($\Lambda(10^{-3}\,M)= 27\ \Omega^{-1}\ cm^2\ mol^{-1}$). Suitable elemental analysis results could not be obtained on the solid product due to its hygroscopic nature.

(f) $[Rh_2(CO)_2(\mu\text{-}S)(dmpm)_2]$ (9). To a 100-mg sample of *trans*-$[RhCl(CO)(dmpm)]_2$ (**1**) (0.165 mmol) dissolved in CH_2Cl_2 (10 mL) was added $Na_2S{\bullet}9H_2O$ (80 mg, 0.33 mmol) and 98% ethanol (10 mL). After stirring the solution for 3 h the solvents were removed in vacuo and the product redissolved in a minimum volume of CH_2Cl_2 (ca. 8 mL). A red solution resulted upon addition of diethyl ether (25 mL), cooling to 0°C, and filtrating the mixture through a pad of Celite. The solvents were again removed in vacuo and the residue redissolved in CH_2Cl_2 (ca. 8 mL). Hexane (30 mL) was added, the solution was cooled to 0°C and filtered through a pad of Celite to remove a small amount of brown precipitate. Complex **9** was obtained in high purity (established by $^{31}P\{^1H\}$ NMR) as a red solid in 62% yield (58 mg) upon removal of the solvents in vacuo.

(g) $[Rh_2Cl_2(CO)_2(\mu\text{-}DMAD)(dmpm)_2]$ (11). Dimethyl acetylenedicarboxylate (DMAD) (20 µL, 0.16 mmol) was added via syringe to a solution of *trans*-$[RhCl(CO)(dmpm)]_2$ (**1**) (100 mg, 0.165 mmol) dissolved in CH_2Cl_2 (10 mL). This resulted in an immediate colour change from orange-red to yellow. Stirring was continued for 30 min after which the solvent volume was reduced (ca. 5 mL) in vacuo, diethyl ether was added

(25 mL) and the solution was cooled to °C. The solvents were removed by cannula under positive N_2 pressure, the light yellow solid was washed with diethyl ether, dried in vacuo and collected in 85% yield (104 mg). Anal. Calcd for $C_{18}Cl_2H_{34}O_6P_4Rh_2$: C, 28.9%; Cl, 9.5%; H, 4.6%. Found: C, 28.6%; Cl, 9.1%; H, 5.0%.

(h) [$Rh_2Cl_2(CO)_2(\mu$-HFB)(dmpm)$_2$] (12). A 100-mg sample of *trans*-[RhCl(CO)(dmpm)]$_2$ (**1**) (0.165 mmol) dissolved in CH_2Cl_2 (12 mL) was placed under an atmosphere of hexafluoro-2-butyne (HFB). The solution underwent an immediate colour change from red-orange to yellow. Stirring of the solution was continued under a static atmosphere of HFB for 30 min after which time the solvent volume was reduced to ca. 5 mL under dinitrogen, diethyl ether was added, and the solution cooled to 0°C. The solvents were removed by cannula under positive N_2 pressure, the bright yellow solid was dried under dinitrogen and collected in 85% yield (108 mg). Anal. Calcd for $C_{16}Cl_2F_6H_{28}O_2P_4Rh_2$: C, 25.0%; Cl, 9.3%; H, 3.6%. Found: C, 25.1%; Cl, 9.0%; H, 3.7%.

(i) [$Rh_2Cl(CO)_2(\mu$-DMAD)(dmpm)$_2$][BF_4] (13). Method A. A 100 mg sample of [$Rh_2Cl_2(CO)_2(\mu$-DMAD)(dmpm)$_2$] (**11**) (0.134 mmol) was suspended in THF (20 mL) and a solution of $AgBF_4$ (26 mg, 0.13 mmol) in THF (10 mL) was added by syringe. The reaction mixture was stirred for 60 min over which time a fine white precipitate of silver chloride formed. The solvent was removed under vacuum, the product redissolved in CH_2Cl_2 (15 mL) and the solution filtered through a pad of Celite. The volume of the orange-yellow solution was reduced ca. 8 mL in vacuo, diethyl ether was added (25 mL) and the solution cooled to 0°C. Removal of the solvents by cannula under positive N_2 pressure, washing with diethyl ether and drying under vacuum afforded a yellow solid identified as compound **13** in 90% yield (96 mg). Compound **13** was determined to be a 1:1 electrolyte in nitromethane solution ($\Lambda(10^{-3}\ M) = 86\ \Omega^{-1}\ cm^2\ mol^{-1}$). Anal. Calcd for $BC_{18}ClF_4H_{34}O_6P_4Rh_2$: C, 27.1%; Cl, 4.4%; H, 4.3%. Found: C, 27.2%; Cl, 4.7%; H, 4.3%.

Method B. Dimethyl acetylenedicarboxylate (10 µL, 0.083 mmol) was added to a solution of $[Rh_2(CO)_2(\mu\text{-}Cl)(dmpm)_2][BF_4]$ (**4**) (54 mg, 0.083 mmol based upon 100% conversion of 50 mg of compound **1**) in CH_2Cl_2 (12 mL). After stirring for 40 min the solvent volume was reduced to ca. 6 mL under vacuum, diethyl ether added (25 mL), the solution cooled to 0°C and the solvents removed by cannula under positive N_2 pressure. The yellow solid was dried in vacuo and collected in 74% yield (49 mg).

(j) $[Rh_2Cl(CO)_2(\mu\text{-}HFB)(dmpm)_2][BF_4]$ (14). Method A. Compound **14** was prepared in a manner analogous to that of **13** but using 100 mg of $[Rh_2Cl_2(CO)_2(\mu\text{-}HFB)(dmpm)_2]$ (**12**) (0.130 mmol) in 15 mL of THF and $AgBF_4$ (25.4 mg, 0.130 mmol) dissolved in 10 mL of THF. Compound **14** was obtained as a yellow-orange solid in 91% yield (97 mg) upon drying under vacuum. The product was determined to be a 1:1 electrolyte in nitromethane solution ($\Lambda(10^{-3}\ M) = 63\ \Omega^{-1}\ cm^2\ mol^{-1}$). Anal. Calcd for $BC_{16}ClF_{10}H_{28}O_2P_4Rh_2$: C, 23.5%; Cl, 4.3%; H, 3.4%. Found: C, 23.2%; Cl, 4.6%; H, 3.5%.

Method B. Compound **14** was prepared in a manner analogous to that of **13** (method B) by placing an atmosphere of HFB over a CH_2Cl_2 solution of compound **4** (54 mg, 0.083 mmol based on 100% conversion of

50 mg of compound **1**); yield 71% (48 mg).

Reaction of $[Rh_2(CO)_2(\mu\text{-}Cl)(dmpm)_2][BF_4]$ (4) with CO. A solution of complex **4** was prepared in the manner described above using 50 mg (0.083 mmol) of *trans*-$[RhCl(CO)(dppm)]_2$ (**1**) and $AgBF_4$ (16.1 mg, 0.083 mmol). Carbon monoxide was then passed through a CH_2Cl_2 solution of **4** for 1 min. The resulting product $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(dmpm)_2][BF_4]$ (**6**) rapidly lost CO when placed under an atmosphere of N_2 and was therefore stored in solution under an atmosphere of CO. Characterization of this species was undertaken by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR solution spectroscopy (see Tables 2.1 and 2.2).

Reaction of $[Rh_2(CO)_2(\mu\text{-}Br)(dmpm)_2][BF_4]$ (5) with CO. A solution of compound **5** was prepared in the manner described above using 50 mg (0.072 mmol) of *trans*-$[RhBr(CO)(dppm)]_2$ and $AgBF_4$ (14.0 mg, 0.072 mmol). Carbon monoxide was then passed through a CH_2Cl_2 solution of **5** for 1 min. The resulting product $[Rh_2(CO)_2(\mu\text{-}Br)(\mu\text{-}CO)(dmpm)_2][BF_4]$ (**7**) lost CO slowly with time when placed under a dinitrogen atmosphere and was therefore stored in solution under an atmosphere of CO. Characterization of this species was undertaken by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR solution spectroscopy (see Tables 2.1 and 2.2).

$^{31}P\{^1H\}$ NMR Magnetization Transfer Experiments. The cationic dicarbonyl species $[Rh_2(CO)_2(\mu\text{-}Cl)(diphosphine)_2][BF_4]$ (diphosphine= dmpm, dppm) were prepared from *trans*-$[RhCl(CO)(diphosphine)]_2$ by the removal of a chloride ligand using one equivalent of $AgBF_4$ in THF solution. After isolation, each compound was redissolved in CD_2Cl_2, the solution placed in a 5 mm NMR tube and less than one equivalent of CO

Table 2.1. Infrared Spectroscopic Data for the Compounds in Chapter 2.[a]

		Nujol, cm^{-1}		CH_2Cl_2 solution, cm^{-1}	
no.	compound	ν(CO)	ν(CC)	ν(CO)	ν(CC)
1	*trans*-$[RhCl(CO)(dmpm)]_2$	1956(vs)		1965(s)	
2	*trans*-$[RhBr(CO)(dmpm)]_2$	1961(m, sh), 1954(s)		1966(vs)	
3	$[RhCl_2(CO)(dmpm)]_2$	2039(vs)		2044(vs)	
4	$[Rh_2(CO)_2(\mu\text{-}Cl)(dmpm)_2][BF_4]$	1986(vs), 1958(vs)		1997(s), 1980(s)	
5	$[Rh_2(CO)_2(\mu\text{-}Br)(dmpm)_2][BF_4]$	1987(s, br), 1960(s, br)		1997(m), 1979(s) 1991(m),[b] 1973(s)[b]	
6	$[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(dmpm)_2][BF_4]$			2057(w), 1997(s), 1990(w), 1860(w), 1710(w)	

Table 2.1. (continued)

7	$[Rh_2(CO)_2(\mu\text{-}Br)(\mu\text{-}CO)(dmpm)_2][BF_4]$	1969(s, br), 1940(m, br),		1978(s, br), 1862(m)	
		1852(s)			
9	$[Rh_2(CO)_2(\mu\text{-}S)(dmpm)_2]$	1932(s), 1916(s)		1925(s), 1941(s)	
11	$[Rh_2Cl_2(CO)_2(\mu\text{-}DMAD)(dmpm)_2]$	2028(vs), 2005(vs)	1562(m)	2035(s), 2025(s)	1571(w)
		1712(m),[c] 1665(s)[c]		1702(m),[c] 1679(m)[c]	
		1980(vs),[d] 1958(vs)[d]			
12	$[Rh_2Cl_2(CO)_2(\mu\text{-}HFB)(dmpm)_2]$	2030(vs)	1590(m)	2039(s)	1590(w)
13	$[Rh_2Cl_2(CO)_2(\mu\text{-}DMAD)(dmpm)_2][BF_4]$	2036(s), 2023(s)	1561(m)	2048(s), 2020(sh)	1567(br)
		1687(br)[c]		1690(br)[c]	
14	$[Rh_2Cl(CO)_2(\mu\text{-}HFB)(dmpm)_2][BF_4]$	2045(vs)	1597(m)	2059(s)	1602(m)

[a] Abbreviations used: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; br, broad. [b] THF solution. [c] ν(CO) of CO_2Me. [d] ν(^{13}CO).

Table 2.2. NMR Spectroscopic Data for the Compounds in Chapter 2.^{a,b}

compound	$\delta(^{31}P\{^1H\})^c$	$\delta(^{13}C\{^1H\})^d$	$\delta(^1H)$		
			P-CH_3	-CH_2-	others
1	-3.56(d, 116 Hz)	189.0(dt, $^1J_{C\text{-}Rh}$= 59.1 Hz,	1.71(t, 12H, J= 3 Hz),	2.46(q, 4H, J= 4.6 Hz)	
		$^2J_{C\text{-}P}$ = 16.5 Hz)	1.66(dt, 12H, J= 1.2, 3.2 Hz)		
2	-6.42(d, br, 114 Hz)		1.81(s, 12H), 1.68(s, 12H)	2.53(s, br, 4H)	
	-5.52(d, 112 Hz)^e				
3	-2.92(d, 84 Hz)		1.89(s, 24H)	3.04(q, 4H, J= 5 Hz)	
4	-4.74(d, 106 Hz)	185.6(dt, $^1J_{C\text{-}Rh}$= 82.6 Hz,	1.73(m, 12H)	2.87(dq, 2H), 2.26 (dq, 2H)	
		$^2J_{C\text{-}P}$ = 17.2 Hz)^f	1.69(m, 12H)		
5	-5.95(d, br, 104 Hz)		1.73(s, 24H)	3.03(m, br, H), 2.50(m, br, 2H),	
	-5.66(d, 104 Hz)^g		1.65(s, 24H)^g	2.97(m, 2 H),^{g} 2.43(m, 2 H)^g	
6	0.18(d, 96 Hz)^f	192.8(m), 188.7(m)^f			
7	9.2(d, br, 85 Hz)		1.78(s, 24H)	2.70(m, br, 4H)	
	11.98(d, 89 Hz)^g				
9	-10.74(d, 120.8 Hz)	185.2(s),	1.74(t, 12H), 1.59(s, 12H)	3.57(dq, 2H),1.90(dq, 2H)	
		183.8(dt, $^1J_{C\text{-}Rh}$= 69.2 Hz, $^2J_{C\text{-}P}$ = 15.2 Hz)^h			

Table 2.2. (continued)

11	-8.55(dt, 97, 27 Hz), -6.25(dt, 90, 26 Hz)	191.2(dt, $^1J_{C-Rh}$= 55.2 Hz, $^2J_{C-P}$= 14.5 Hz), 175.7(m, $^1J_{C-Rh}$= 56.4 Hz, $^2J_{C-Rh}$= 12.4 Hz)	1.54(t, 6H, J= 3 Hz), 1.70(t, 6H, J= 4 Hz), 1.76(t, 6H, J= 3.5 Hz), 1.82(t, 6H, J= 3.5 Hz)	2.64 (m, 2H), 2.81(m, 2H)	3.65(s, -OCH$_3$)
12	-8.07(dt, 96, 28 Hz), -6.11(dt, 92, 29 Hz)		1.61(t, 6H, J= 3 Hz), 1.63(t, 6H, J= 3 Hz), 1.79(t, 6H, J= 3 Hz), 1.85(t, 6H, J= 3 Hz)	2.77(m, 2H), 2.88(m, 2H)	
13	-6.47(d, 91 Hz) -5.77(dt, 85, 25 Hz),[e] -9.96(dt, 86, 25 Hz)[e]		1.84(s, 12H), 1.66(s, 12H)	2.75(m, 2H), 2.50(m, 2H)	3.68(s, -OCH$_3$)
14	-5.82(d, 89) -5.10 dt (83, 26 Hz),[e] -7.45 dt (103, 25 Hz)[e]		1.88(s, 12H), 1.68(s, 12H)	2.55(q, 4H)	

[a] Ambient temperature in CD_2Cl_2 unless otherwise noted. [b] Abbreviations used: s, singlet; d, doublet; t, triplet; q, quintet; dt, doublet of triplets; dq, doublet of quintets; m, multiplet.; br, broad. [c] Vs 85% H_3PO_4, numbers in parentheses represent the separation in hertz between the major peaks in the second-order spectrum of the complex. [d] ^{13}CO enriched samples. [e] -40°C. [f] -60°C. [g] -75°C. [h] -93°C.

added via a gas tight syringe. The $^{31}P\{^1H\}$ NMR spectrum of each sample, taken at -58°C, contained two second order signals, one due to the dicarbonyl starting material and a lower field signal due to the tricarbonyl product. The soft pulse transfer experiments were performed on these samples using a Bruker AM-400 spectrometer and the rate of exchange results were calculated using non-linear least squares analysis at the University of Alberta Computing Services. The inversion experiments and calculations were performed using the method described by Alger and Prestegard.[21] The required frequencies for pulsing were derived using a PTS 160 frequency synthesizer. Typical 180° pulse times were 92 μs. For each run a total of fifteen 90° observation pulses were taken at delays ranging from 5.0×10^{-5} s to 3.0 s.

The rate of CO loss from the tricarbonyl species at -58°C, as shown in equation 2.1, was found to be $k_{21} = 3.6 \text{ s} \pm 0.4 \text{ s}$ for diphosphine = dmpm and $k_{21} = 0.35 \text{ s} \pm 0.14 \text{ s}$ for diphosphine = dppm.

$$[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(diphosphine)_2]^+ \xrightarrow[-CO]{k_{21}} [Rh_2(CO)_2(\mu\text{-}Cl)(diphosphine)_2]^+ \tag{2.1}$$

X-Ray Data Collection. Red crystals of $[Rh_2Cl_4(CO)_2(dmpm)_2]\bullet CH_2Cl_2$ (3) were obtained by serendipity upon attempts to obtain crystals of compound **1** via the diffusion of diethyl ether into a saturated CH_2Cl_2 solution of *trans*-$[RhCl(CO)(dmpm)]_2$. Data were collected on an Enraf-Nonius CAD4 diffractometer at 22°C using graphite-monochromated MoKα radiation. The automatic peak search and reflection indexing programs, in conjunction with a cell reduction program, established the orthorhombic crystal system, and the systematic absences unambiguously established the space group as *Pbcn*. Cell constants were obtained from a least-squares refinement of the setting angles (centered in both positive and negative theta) of 25 reflections having 2θ between 21.90° and 25.78°.

The intensity data were collected by using the $\theta/2\theta$ scan technique with variable scan speeds chosen to give $\sigma(I)/I \leq 0.03$ within a time limit of 50 s in order to achieve improved counting statistics for both intense and weak reflections in a minimum time. The scan range was determined as a function of θ to compensate for the α_1-α_2 wavelength dispersion and backgrounds for the peaks were measured by extending the scan 25% on either side of the calculated range. Three reflections were chosen as standard reflections and were remeasured every 60 min of exposure time to check on crystal and electronic stability over the course of data collection. There was no noticeable decrease in the intensity of the standards so no correction was applied. See Table 2.3 for crystal data and details of intensity collection. The data were corrected for Lorenz and polarization effects and for absorption using the method of Walker and Stuart.[22,23] Data were reduced in the usual manner by using a value of $p = 0.04$ to downweight intense reflections.[24]

Results and Discussion

(a) Carbonyl Complexes. The reaction of $[RhCl(cod)]_2$ with carbon monoxide and two equivalents of dmpm in refluxing acetone yields a red-orange product assigned as *trans*-$[RhCl(CO)(dmpm)]_2$ (**1**). A similar

Table 2.3. Crystallographic Data for $[Rh_2Cl_4(CO)_2(dmpm)_2]\cdot CH_2Cl_2$ (3).

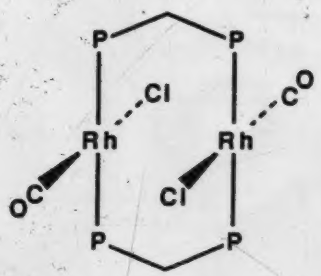
compound	$[Rh_2Cl_4(CO)_2(dmpm)_2]\cdot CH_2Cl_2$
formula weight	760.81
formula	$C_{13}Cl_6H_{30}O_2P_4Rh_2$
crystal shape	irregular
crystal dimensions, mm	0.36 × 0.37 × 0.47
systematic absences	*0kl*, *k* odd; *h0l*, *l* odd; *hk0*, *h+k* odd
space group	*Pbcn* (No. 60)
temperature, °C	22
radiation (λ, Å)	graphite-monochromated Mo Kα (0.71069)
unit cell parameters	
a, Å	30.573 (4)
b, Å	13.469 (2)
c, Å	12.624(2)
V, Å^3	5198.8
Z	8
ρ(calcd), g cm^{-3}	1.944
linear absorption coeff (μ), cm^{-1}	21.28
range of transmission factors	0.848 - 1.148
detector aperture, mm	3.00 + (tan θ) wide × 4.00 high
takeoff angle, deg	3.0

Table 2.3. (continued)

maximum 2θ, deg	52.0
crystal-detector distance, mm	173
scan type	$\theta/2\theta$
scan rate, deg/min^{-1}	between 1.00 and 6.67
scan width, deg	$0.50 + 0.347 \tan \theta$
total unique reflections	5674 ($+h$,$+k$, $+l$)
total observations (NO)	3985
final no. parameters varied (NV)	239
error in obs. of unit wt. (GOF)[a]	1.629
R^b	0.044
$R_w{}^c$	0.058

[a] $\mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$. [b] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.
[c] $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o{}^2]^{1/2}$.

procedure for the preparation of complex **1** has recently been reported.[25] Based on the spectroscopic parameters, it appears that **1** has a geometry in which the chloro ligands (and the carbonyls) have a mutually trans arrangement on adjacent metals, as illustrated. The $^{31}P\{^1H\}$ NMR spectrum of compound **1** is shown in Figure 2.1 and appears at δ -3.56 as a symmetrical, second order multiplet with a separation of 116 Hz between the two principal peaks. Such a second order pattern, which is dominated by two major peaks, is typical of the $^{31}P\{^1H\}$ NMR spectra of symmetrical dirhodium complexes found in this work and previously for related "$Rh_2(dppm)_2$" compounds.[12b,12c,12d,14a,14c,14d,14f,15,16] In particular, the signal for compound **1** is very similar to that of the closely related compound, $[Rh_2(CO)_2(\mu\text{-}Cl)(dppm)_2]^+$.[12b,14a] The exactly analogous dppm species, *trans*-$[RhCl(CO)(dppm)]_2$ is highly insoluble in all common solvents so its solution spectrum has not been obtained.[12a]



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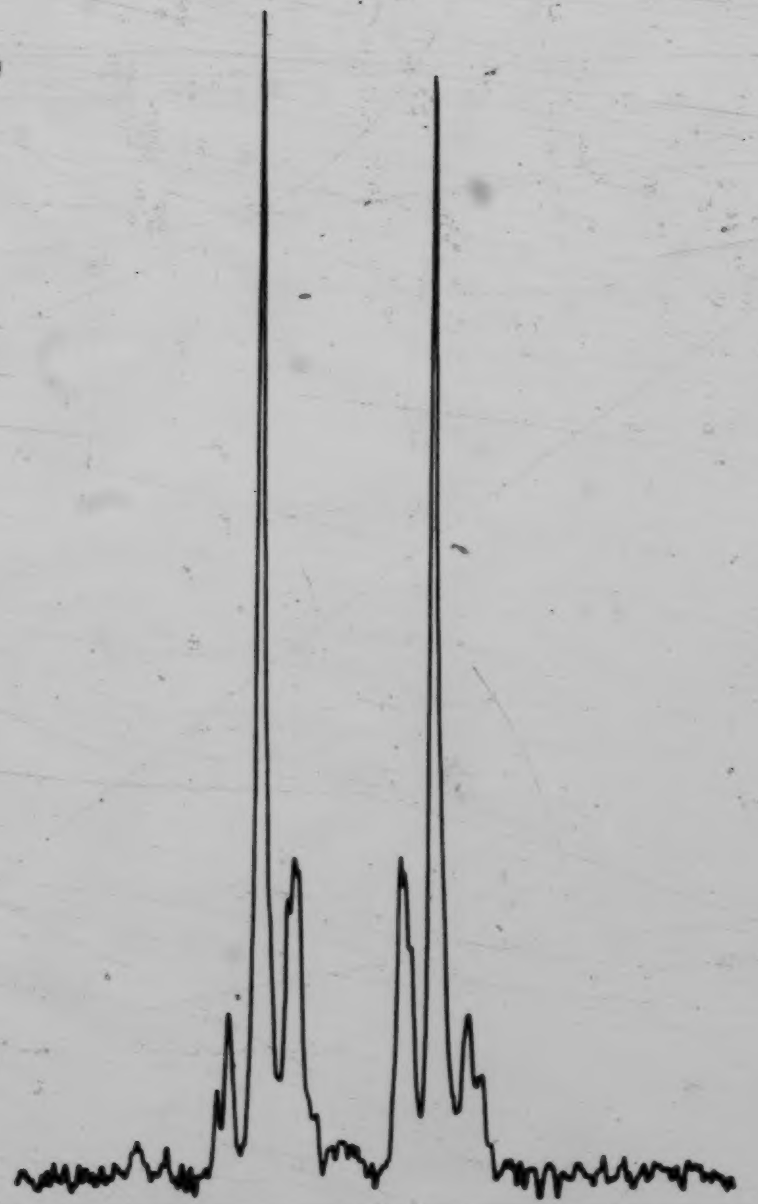

Figure 2.1. The $^{31}P\{^1H\}$ NMR spectrum of *trans*-[RhCl(CO)(dmpm)]$_2$ (1) at 25°C.

The single carbonyl stretch in the infrared spectrum of **1**, at 1956 cm^{-1} (Nujol), is consistent with the proposed trans geometry and is somewhat lower in frequency than that observed for the dppm counterpart ($\nu(CO) = 1976\ cm^{-1}$, Nujol).[12a] This frequency shift is accordant with the presumed greater basicity of the dmpm ligand,[6] which gives rise to increased π back-donation to the carbonyl groups from the metal centres. Although the preparation of complex **1** succeeds equally well in a number of other solvents (dichloromethane, tetrahydrofuran or toluene) the low solubility of the product in acetone provides an easy means for its isolation in high yield and purity.

The chemistry reported above, for the dmpm ligand, parallels that of rhodium involving the related dppm group in which a similar dicarbonyl-rhodium species was obtained,[13] but contrasts to the dppm-bridged iridium chemistry in which the species isolated under similar conditions was the tetracarbonyl complex, $[Ir_2Cl(CO)_4(dppm)_2][Cl]$.[18b] This diiridium tetracarbonyl species did ultimately yield the analogous dicarbonyl product, *trans*-$[IrCl(CO)(dppm)]_2$, through stepwise CO loss, but forcing conditions were required to eliminate the extra carbonyl groups. We had originally anticipated that with the basic dmpm ligand higher carbonyl complexes of rhodium might be obtained, possibly analogous to those involving the "$Ir_2(dppm)_2$" system, however this was not the case, at least under these conditions.

The reaction of complex **1** with excess NaBr provides the bromide analogue *trans*-$[RhBr(CO)(dppm)]_2$ (**2**). Spectroscopically, compound **2** is similar in all respects to compound **1** with only slight variations in ^1H and

$^{31}P\{^1H\}$ NMR chemical shifts and infrared ν(CO) values (see Tables 2.1 and 2.2). Based on this similarity we propose that this bromide species has the same face-to-face geometry illustrated for compound **1** with the bromide and carbonyl ligands trans to each other. This configuration is also that which has been presumed for the dpam (bis(diphenylarsino)methane) analogue $[RhBr(CO)(dpam)]_2$.[12a] In contrast to the "$Rh_2(dmpm)_2$" formulation, the reaction of NaBr with the dppm analogue of **1** initially yields the asymmetric species $[Rh_2Br_2(CO)(\mu\text{-}CO)(dppm)_2]$ [14g] (originally reported to be a cationic species).[14d] This product subsequently loses CO in solution, providing the A-frame species $[Rh_2Br_2(\mu\text{-}CO)(dppm)_2]$.[14d,14e] Although the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture of **1** and NaBr reveals a significant amount of impurities, we have been unable to isolate or characterize in solution any asymmetric compound which corresponds to the dppm product. We note that the low conductivity value of pure compound **2** in solution (THF, $\Lambda(10^{-3}\ M)= 0.8\ \Omega^{-1}\ cm^2\ mol^{-1}$) is consistent with the presence of only nonelectrolyte species. Also, the heating of complex **2** in acetone for several hours did not result in the loss of CO and formation of the monocarbonyl A-frame counterpart of the dppm complex.

The formation of a symmetrical dibromide compound, **2**, is consistent with steric bulk arguments made regarding the structural trend observed for the dppm and dpam bromide species mentioned above.[14d] This argument is based on the structures of compounds $[RhX(CO)(P\text{-}P)]_2$ (X= Cl, Br, I; P-P= dppm, dpam). Members of this series containing smaller halides (X= Cl, P-P= dppm; X= Cl, Br, P-P= dpam) are neutral species and possess the symmetric trans geometry.[12a,14d] When bulkier halides are present (X= Br, I, P-P= dppm),[14d] the configuration of the equatorial ligands is apparently destabilized and an unsymmetrical, A-frame species such as [Rh_2Br_2(CO)(μ-CO)$(dppm)_2$] is formed,[14g] presumably to help relieve the steric congestion in the face-to-face structure. It is therefore not unreasonable to assume that the geometry of complex **2** can be explained as a result of the lesser steric requirements of dmpm (relative to dppm and dpam) which allow sufficient space for the trans arrangement of larger ligands in the equatorial plane. Puddephatt and coworkers have made similar statements regarding the platinum dimers $[PtXMe(P\text{-}P)]_2$ which are neutral when P-P= dmpm but ionic when P-P= dppm (X= Cl, I).[9d]

Compound **1** reacts immediately with one equivalent of thionyl chloride to yield the tetrachloride species $[RhCl_2(CO)(dmpm)]_2$ (**3**). This complex was first obtained unintentionally from a solution of **1** in CH_2Cl_2/diethyl ether which had been set aside in an attempt to obtain suitable crystals of **1** for an X-ray study. Instead, well formed red single crystals of complex **3** were obtained. The species analyzed as the tetrachloride, and had a carbonyl stretch at 2039 cm^{-1}, consistent with the proposed Rh(II) formulation. All spectroscopic data for this complex are straight forward (see Tables 2.1 and 2.2). An X-ray structure determination of this species indicates that it has the structure shown in Figure 2.2, resulting from the apparent oxidative addition of Cl_2 to *trans*-[RhCl(CO)-$(dmpm)]_2$ (**1**). Positional and thermal parameters, bond lengths, and angles are given in Tables 2.4, 2.5 and 2.6, respectively. Compound **3** had been observed on previous occasions when **1** had been exposed to chlorinated

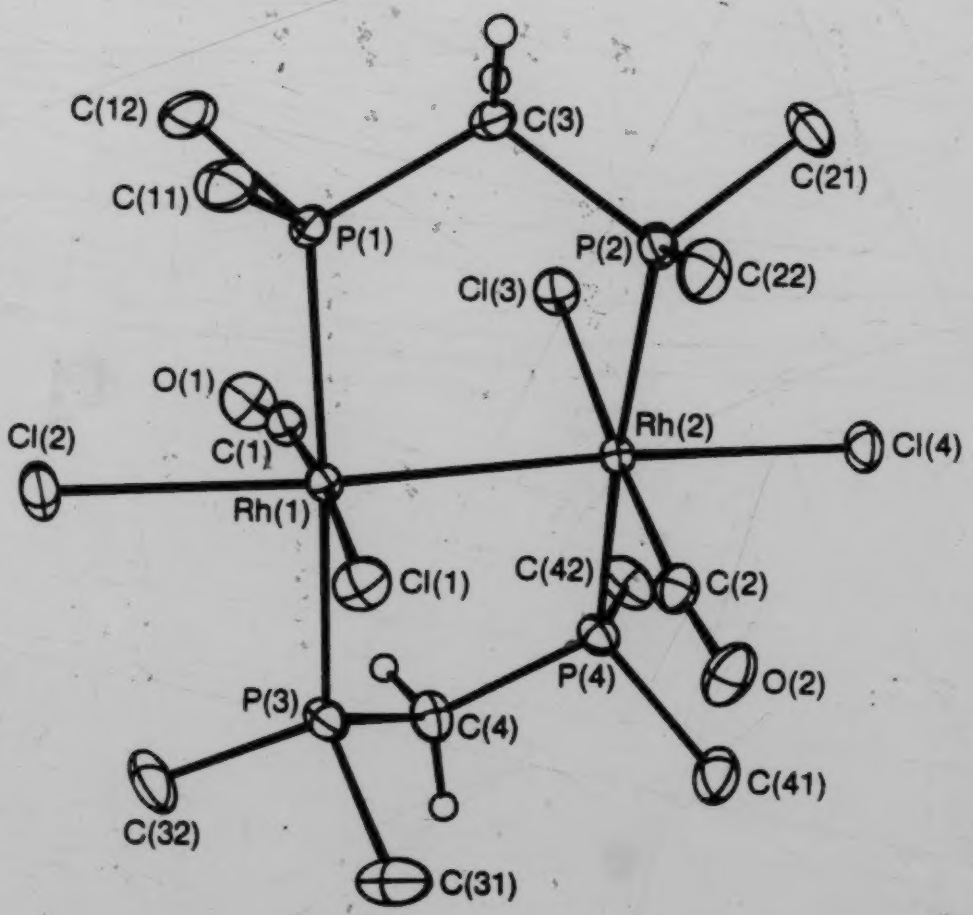

Figure 2.2. A perspective view of $[Rh_2Cl_4(CO)_2(dmpm)_2]$ (3) showing the numbering scheme. Thermal parameters are shown at the 20% level except for methylene hydrogens which are drawn artifically small. Hydrogen atoms on the methyl groups are omitted for the sake of clarity.

Table 2.4. **Positional and Thermal Parameters for $[Rh_2Cl_4(CO)_2(dmpm)_2]\cdot CH_2Cl_2$ (3).**[a, b]

Atom	*x*	*y*	*z*	*B* (e/Å^2)
Rh(1)	0.16210(2)	0.19977(4)	0.08078(4)	1.980(9)
Rh(2)	0.10726(2)	0.30283(4)	0.21506(4)	1.958(9)
Cl(1)	0.10442(6)	0.1236(1)	-0.0170(1)	3.23(4)
Cl(2)	0.21570(6)	0.1185(1)	-0.0385(2)	3.92(4)
Cl(3)	0.16261(6)	0.4237(1)	0.2514(2)	3.26(4)
Cl(4)	0.05757(6)	0.3864(1)	0.3419(1)	3.37(4)
Cl(5)[c]	-0.325(3)	0.2317(6)	-0.176(1)	17.8(4)
Cl(6)[c]	-0.0026(3)	0.0838(8)	-0.176(1)	17.8(4)
P(1)	0.16400(5)	0.3315(1)	-0.0414(1)	2.28(3)
P(2)	0.08555(6)	0.4077(1)	0.0777(1)	2.56(4)
P(3)	0.16371(6)	0.0667(1)	0.2004(2)	2.88(4)
P(4)	0.12698(6)	0.2078(1)	0.3637(1)	2.72(4)
O(1)	0.2416(2)	0.2704(4)	0.1930(5)	4.6(1)
O(2)	0.0330(2)	0.1678(4)	0.1658(5)	4.3(1)
C(1)	0.2096(2)	0.2508(5)	0.1530(6)	2.9(1)
C(2)	0.0627(2)	0.2155(5)	0.1821(5)	2.8(1)
C(3)	0.1315(2)	0.4405(5)	-0.0047(6)	2.8(1)
C(4)	0.1670(2)	0.1098(6)	0.3373(6)	3.2(2)
C(5)[c]	0.016(1)	0.186(2)	-0.224(5)	22(1)*
C(11)	0.1472(3)	0.2985(6)	-0.1755(6)	4.1(2)

Table 2.4. (continued).

C(12)	0.2173(2)	0.3843(6)	-0.612(8)	4.7(2)
C(21)	0.0642(3)	0.5250(5)	0.1217(6)	3.9(2)
C(22)	0.0442(2)	0.3635(6)	-0.0121(6)	3.7(2)
C(31)	0.1186(3)	-0.0200(6)	0.1879(8)	5.4(2)
C(32)	0.2111(3)	-0.0134(6)	0.1879(8)	5.4(2)
C(41)	0.0816(3)	0.1441(7)	0.4239(7)	5.1(2)
C(42)	0.1513(3)	0.2751(6)	0.4728(6)	4.5(2)

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[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab\ (\cos \text{gamma})\beta_{12} + ac\ (\cos \text{beta})\beta_{13} + bc\ (\cos \text{alpha})\beta_{23}]$. [b] Numbers in parentheses in this and all subsequent tables are estimated standard deviations in the least signficant digits.
[c] Disordered CH_2Cl_2.

Table 2.5. Bond Distances (Å) in $[Rh_2Cl_4(CO)_2(dmpm)_2]\cdot CH_2Cl_2$ (3).[a]

Rh(1)-Rh(2)	2.7591(5)	P(1)-C(11)	1.824(6)
Rh(1)-Cl(1)	2.385(1)	P(1)-C(12)	1.795(6)
Rh(1)-Cl(2)	2.480(1)	P(2)-C(3)	1.804(5)
Rh(1)-P(1)	2.352(1)	P(2)-C(21)	1.797(6)
Rh(1)-P(3)	2.344(1)	P(2)-C(22)	1.800(6)
Rh(1)-C(1)	1.847(6)	P(3)-C(4)	1.826(6)
Rh(2)-Cl(3)	2.393(1)	P(3)-C(31)	1.806(7)
Rh(2)-Cl(4)	2.478(1)	P(3)-C(32)	1.814(6)
Rh(2)-P(2)	2.333(1)	P(4)-C(4)	1.829(6)
Rh(2)-P(4)	2.351(1)	P(4)-C(41)	1.799(7)
Rh(2)-C(2)	1.846(6)	P(4)-C(42)	1.809(6)
Cl(5)[a]-C(5)	1.67(4)	O(1)-C(1)	1.132(6)
Cl(6)-C(5)	1.61(4)	O(2)-C(2)	1.132(6)
P(1)-C(3)	1.831(5)		

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[a] Atoms Cl(5), Cl(6) and C(5) are from CH_2Cl_2 of crystallization.

Table 2.6. Bond Angles (deg) in $[Rh_2Cl_4(CO)_2(dmpm)_2]\cdot CH_2Cl_2$ (3).

Rh(2)-Rh(1)-Cl(1)	94.89(4)	Cl(3)-Rh(2)-C(2)	176.5(2)
Rh(2)-Rh(1)-Cl(2)	175.33(4)	Cl(4)-Rh(2)-P(2)	91.96(5)
Rh(2)-Rh(1)-P(1)	92.18(4)	Cl(4)-Rh(2)-P(4)	83.62(5)
Rh(2)-Rh(1)-P(3)	90.09(4)	Cl(4)-Rh(2)-C(2)	89.0(2)
Rh(2)-Rh(1)-C(1)	89.2(2)	P(2)-Rh(2)-P(4)	175.03(5)
Cl(1)-Rh(1)-Cl(2)	89.10(5)	P(2)-Rh(2)-C(2)	90.5(2)
Cl(1)-Rh(1)-P(1)	90.20(5)	P(4)-Rh(2)-C(2)	91.3(2)
Cl(1)-Rh(1)-P(3)	91.14(5)	Rh(1)-P(1)-C(3)	115.2(2)
Cl(1)-Rh(1)-C(1)	175.5(2)	Rh(1)-P(1)-C(11)	114.7(2)
Cl(2)-Rh(1)-P(1)	85.35(5)	Rh(1)-P(1)-C(12)	114.3(2)
Cl(2)-Rh(1)-P(3)	92.27(5)	C(3)-P(1)-C(11)	106.1(3)
Cl(2)-Rh(1)-C(1)	86.8(2)	C(3)-P(1)-C(12)	102.1(3)
P(1)-Rh(1)-P(3)	177.25(5)	C(11)-P(1)-C(12)	102.9(3)
P(1)-Rh(1)-C(1)	91.4(2)	Rh(2)-P(2)-C(3)	110.8(2)
P(3)-Rh(1)-C(1)	87.1(2)	Rh(2)-P(2)-C(21)	113.9(2)
Rh(1)-Rh(2)-C(12)	91.74(4)	Rh(2)-P(2)-C(22)	117.9(2)
Rh(1)-Rh(2)-C(13)	176.65(4)	C(3)-P(2)-C(21)	104.3(3)
Rh(1)-Rh(2)-P(2)	91.20(4)	C(3)-P(2)-C(22)	105.4(3)
Rh(1)-Rh(2)-P(4)	93.47(4)	C(21)-P(2)-C(22)	103.4(3)
Rh(1)-Rh(2)-C(2)	89.4(2)	Rh(1)-P(3)-C(4)	111.6(2)
Cl(3)-Rh(2)-Cl(4)	90.04(5)	Rh(1)-P(3)-C(31)	118.8(2)
Cl(3)-Rh(2)-P(2)	86.09(5)	Rh(1)-P(3)-C(32)	114.5(3)
Cl(3)-Rh(2)-P(4)	92.06(5)	C(4)-P(3)-C(31)	104.0(3)

Table 2.6. (continued).

C(4)-P(3)-C(32)	103.2(3)	Rh(1)-C(1)-O(1)	170.4(5)
C(31)-P(3)-C(32)	103.1(4)	C(41)-P(4)-C(42)	103.6(3)
Rh(2)-P(4)-C(4)	114.7(2)	Rh(2)-C(2)-O(2)	174.1(5)
Rh(2)-P(4)-C(41)	113.5(2)	P(1)-C(3)-P(2)	111.8(3)
Rh(2)-P(4)-C(42)	116.1(2)	P(3)-C(4)-P(4)	111.5(3)
C(4)-P(4)-C(41)	104.5(3)	Cl(5)-C(5)-Cl(6)[a]	84.(2)
C(4)-P(4)-C(42)	103.1(3)		

[a] Atoms Cl(5), Cl(6) and C(5) are from CH_2Cl_2 of crystallization.

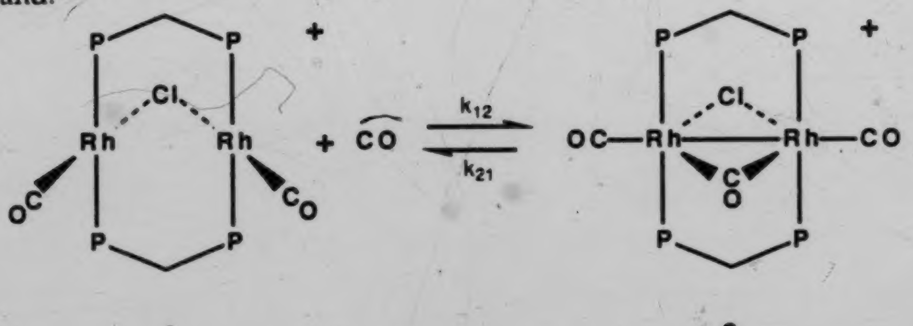
solvents (CH_2Cl_2, $CHCl_3$) for extended periods of time, and could also be prepared directly as the major species by the reaction of **1** with HCl or Cl_2 (the other minor products in these reactions were not identified).

By contrast the analogous compound *trans*-$[RhCl(CO)(dppm)]_2$ was not observed to form the oxidative addition product by chlorine abstraction from solvent. Such a difference is consistent with the more basic dmpm-bridged complex **1** favoring oxidative addition. The dppm analogue has, however, been prepared from the reaction $[Rh_2Cl_2(\mu\text{-}Cl)(\mu\text{-}CO)(dppm)_2][PF_6]$ with tetra-*n*-butylammonium chloride followed by CO [15] or from the reaction of *trans*-$[RhCl(CO)(dppm)]_2$ with $PhICl_2$.[16] The structure of this complex is presumed to be analogous to that of compound **3**. The carbonyl stretching vibration of the dppm complex ($\nu(CO)$= 2041 cm^{-1}, Nujol; 2047 cm^{-1}, CH_2Cl_2) is only slightly higher in frequency than that of compound **3** ($\nu(CO)$= 2039 cm^{-1}, Nujol; 2044 cm^{-1}, CH_2Cl_2), suggesting that the amount of Rh-CO π back-bonding in both compounds are very similar. In spite of this, the dppm species readily loses CO in solution while **3** does not. We consider the possibility that the easy dissociation of CO in the dppm compound may be a consequence of greater steric congestion about the metal centres, created by the more bulky dppm ligands.

Compound **3** has the expected trans arrangement of diphosphine ligands bridging the two pseudo-octahedral metal centers. The Rh(1)-Rh(2) separation of 2.7591(5) Å corresponds to a normal single bond as expected for two adjacent Rh(II) centers. There is no obvious difference between the Rh-P distances (range, 2.333(1)-2.352(1) Å) in this dmpm-bridged complex and those of analogous dppm species.[14b,14d,14f] The two Rh-Cl bonds opposite the Rh-Rh bond (2.480(1), 2.478(1) Å) are longer than those cis to it (2.385(1), 2.393(1) Å), consistent with a high trans influence of metal-metal bonds.[18a] Other bond lengths and angles within the complex are essentially as expected. The ligands on each metal are staggered with regards to each other about the Rh-Rh bond with an average torsion angle of 22.0°, in order to minimize non-bonded contacts.

The cationic A-frame complex $[Rh_2(CO)_2(\mu\text{-}Cl)(dmpm)_2][BF_4]$ (**4**) and its bromide counterpart $[Rh_2(CO)_2(\mu\text{-}Br)(dmpm)_2][BF_4]$ (**5**) are readily prepared from compounds **1** and **2** by removal of a halide ion using one equivalent of $AgBF_4$. The conductivity of both products ($\Lambda(10^{-3}$ M$)= 75\ \Omega^{-1}$ cm^2 mol^{-1} in nitromethane for **4**, $\Lambda(10^{-3}$ M$)= 27\ \Omega^{-1}$ cm^2 mol^{-1} in CH_2Cl_2 for **5**) are consistent with one-to-one electrolytes [26] and spectroscopic data (Tables 2.1 and 2.2) are consistent with the halide-bridged, A-frame structure which has previously been reported for the corresponding rhodium and iridium dppm compounds.[12b,14a,14b,18b] Once again the effect of a more basic diphosphine ligand (dmpm) on the rhodium atoms is realized in lower carbonyl stretching frequencies for compound **4** (1986, 1958 cm^{-1}) compared to those of the dppm analogue $[Rh_2(CO)_2(\mu\text{-}Cl)(dppm)_2][BF_4]$ (1995, 1978 cm^{-1})[14b] and for **5** (1987, 1960 cm^{-1}) compared to those of the dppm analogue $[Rh_2(CO)_2(\mu\text{-}Br)(dppm)_2]^+$ (1998, 1978 cm^{-1}).[17] The $^{31}P\{^1H\}$ NMR spectra of each of the compounds reveal a second order doublet with two principal peaks (δ -4.74 for **4**, δ -5.95 for **5**), similar in form to that of compound **1** in Figure 2.1. The somewhat broader appearance of the bromide species resonance indicates some degree of fluxionality in the molecule at ambient temperature. In the low temperature spectrum (-75°C) the resonance becomes fully resolved into a normal second order doublet at δ -5.66 (see Table 2.2).

Both complexes 4 and 5 react reversibly with CO in solution to yield the tricarbonyl species $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(dmpm)_2][BF_4]$ (6) and $[Rh_2(CO)_2(\mu\text{-}Br)(\mu\text{-}CO)(dmpm)_2][BF_4]$ (7), respectively. These reactions are presumed to follow the pathway established for the dppm adduct $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(dppm)_2][BF_4]$ in which the incoming CO molecule binds terminally to one rhodium atom. This is followed by the movement of a terminal carbonyl ligand into the bridged-position to give a symmetrical final product containing a bridging halide and carbonyl ligand.[12b]



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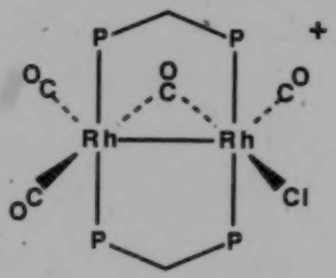
6

Monitoring the addition of CO to complex 4 by $^{31}P\{^1H\}$ NMR spectroscopy at room temperature reveals the presence of a broad apparent doublet at δ -4.47, which upon cooling to -60°C appears as two well defined signals (δ 0.18, -5.67). Both are second order in nature with two principal peaks, characteristic of symmetrical species. The higher field signal is identical in every respect to the starting material and has been assigned as such. The remaining signal at δ 0.18 is attributed to the tricarbonyl species **6** and bears a strong resemblance to the resonance for the dppm analogue.[12b,14a] In addition, the spectra over the temperature range 25° to -60°C are very similar to those observed for the dppm species.[14a] At -60°C the resonance due to the carbonyl groups in ^{13}CO-enriched **4** appears in the $^{13}C\{^1H\}$ NMR spectrum as a doublet of triplets ($^1J_{C\text{-}Rh}$= 82.6 Hz, $^2J_{C\text{-}P}$= 17.2 Hz) at δ 185.6. The addition of ^{13}CO at this temperature results in the appearance of two new unresolved peaks at δ 192.8 and δ 188.7, integrating in the ratio 1:2, respectively. These resonances are consistent with a tricarbonyl species, with the bridging carbonyl ligand appearing at lower field.

Of some surprise to us, the tricarbonyl species **6** loses CO more readily than does its dppm analogue and although $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)\text{-}(dppm)_2]^+$ could be obtained as a solid, compound **6** could not be isolated in pure form due to facile CO loss. In solution, the dicarbonyl starting material **4** and the tricarbonyl product **6** were observed together under an atmosphere of CO. It was subsequently determined by selective inversion magnetization transfer experiments (see Experimental section) that CO loss from **6** occurred at a rate ca. 10 times faster (k_{21}(dmpm)/k_{21}(dppm)= 3.6/0.35) than from the analogous dppm complex $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)\text{-}(dppm)_2][BF_4]$. We had expected that the basic dmpm group would favor binding of strong π-acids and therefore readily add CO to form a stable tricarbonyl species.

Our inability to separate compounds **4** and **6** in solution or in the solid made identification of the carbonyl stretches due to **6** difficult. Careful monitoring of the solution-infrared spectrum of compound **4** upon stepwise CO addition showed that the strong sharp bands at 1997 and 1980 cm^{-1} coalesced to give a broad band at 1997 cm^{-1} with a shoulder at 1990 cm^{-1}. The terminal carbonyl stretches due to both species **4** and **6** are apparently overlapping within this broad envelope. In addition, new bands of weak intensity also appeared at 2057, 1860, and 1710 cm^{-1}. We assign the 1860 cm^{-1} band to the bridging carbonyl ligand of the static structure **6**, and propose that the other bands are due to species involved in some fluxional processes entailing rearrangement of the carbonyl ligands over both metal centres, not unlike that proposed for the dppm species.[14a] The fluxionality of compound **6** should be facilitated by the less bulky methyl substituents on dmpm and although it does not directly follow, it may be at least partially responsible for the more facile removal of CO from this species, compared to its dppm analogue.

The nature of the "$Rh_2(dmpm)_2$" complex which is formed under a CO atmosphere is highly sensitive to slight changes in the CO pressure. Upon flushing CO through the system at atmospheric pressure, such that the reaction vessel atmosphere is completely replaced by CO, a new unsymmetrical species (**8**) appears in the $^{31}P\{^{1}H\}$ NMR spectrum (δ 4.27; CD_2Cl_2 at -60°C) while a new broad undefined peak appears in the $^{13}C\{^{1}H\}$ NMR spectrum (δ 184.6; CD_2Cl_2 at -60°C) when ^{13}CO is used. Replacing the static CO atmosphere above the reaction solution with N_2 apparently lowers the concentration of CO in solution enough to cause the resonance of compound **8** to immediately be replaced by those of **4** and **6**. This extreme lability made it impossible to obtain an infrared spectrum of compound 8 without the presence of major amounts of the dicarbonyl species 4 and the tricarbonyl 6. The only obvious change in the spectra upon addition or removal of CO was the appearance or disappearance of a new weak band at 1807 cm^{-1}. Based on analogies with the well studied "$Ir_2(dppm)_2$" system [18b] we propose that the labile unsymmetrical species 8 is the tetracarbonyl compound shown below. In this instance the basic dmpm ligand would appear to impart enough basicity to the Rh centers to cause some resemblance to the "$Ir_2(dppm)_2$" system; no analogous species was observed upon reaction of $[Rh_2(CO)_2(\mu\text{-}Cl)(dppm)_2]^+$ with carbon monoxide.

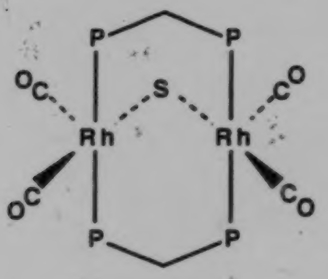


8

The $^{31}P\{^1H\}$ NMR spectrum of the tricarbonyl-bromide species $[Rh_2(CO)_2(\mu\text{-}Br)(\mu\text{-}CO)(dmpm)_2][BF_4]$ (7) under an atmosphere of CO exhibits the same type of broad resonance (δ 9.2) at ambient temperature which was seen for the chloride analogue. The resonance transforms into a well resolved second order doublet at -75°C (δ 11.98), thus confirming the symmetrical nature of the product. An additional resonance of quite weak intensity appears at δ 8.42 (multiplet) which is tentatively assigned to a tetracarbonyl species $[Rh_2Br(CO)_4(dppm)_2][BF_4]$. This signal disappears upon passing N_2 through the NMR sample solution leaving only the resonance due to the tricarbonyl species **7**. Unfortunately, the ease with which CO was lost and the minor amount of this unknown complex that was formed in the first place has precluded its complete characterization. Unlike the tricarbonyl-chloride system there was no evidence in the $^{31}P\{^1H\}$ NMR spectrum of the bromide compound at ambient or low temperature to suggest the presence of the dicarbonyl starting material (**5**) while under a CO atmosphere.

The solution infrared spectrum of compound **7** is much more straight forward than that of the chloride analogue (**6**), having a single terminal and bridging carbonyl stretch at 1978 and 1862 cm^{-1}, respectively (CH_2Cl_2). The uncomplicated appearance of the infrared spectrum implies that the tricarbonyl species does not lose CO as readily as its chloride counterpart. Indeed, we find that passing dinitrogen through a solution of complex **7** does not produce any of the dicarbonyl starting material $[Rh_2(CO)_2(\mu\text{-}Br)(dmpm)_2][BF_4]$ (**5**). However, refluxing of compound **7** in CH_2Cl_2 under dinitrogen for a short period of time does result in some conversion. The easier removal of CO from $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(dmpm)_2][BF_4]$ (**6**) than from $[Rh_2(CO)_2(\mu\text{-}Br)(\mu\text{-}CO)(dmpm)_2][BF_4]$ (**7**) suggests that there is a stronger M-CO interaction for the bromide species. This behavior is consistent with the bromide ligand being a better π-donor than chloride,[27] and is similar to that observed of the dppm analogues where $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(dppm)_2][BF_4]$ was found to lose CO readily,[illegible],[14a] while the bromide compound $[Rh_2(CO)_2(\mu\text{-}Br)(\mu\text{-}CO)(dppm)_2][BF_4]$ lost CO slowly in solution.[14d,17] Upon comparison of ν(CO) values of compound 7 (1969, 1940, 1852 cm^{-1}, Nujol) with it's dppm analogue (2005, 1968, 1865 cm^{-1}, Nujol)[14d] (see also reference 17) we find the former set of values to be significantly lower in frequency than the latter. This difference is consistent with the presumed greater electron-donating ability of dmpm relative to dppm which subsequently increases the M-CO π-backbonding interaction in complex 7, making loss of CO more difficult.

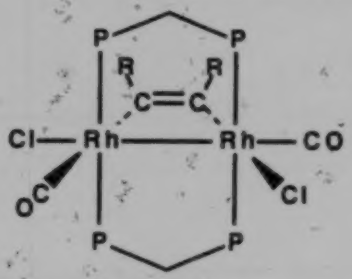
The neutral "A-frame" complex $[Rh_2(CO)_2(\mu\text{-}S)(dmpm)_2]$ (9) is obtained in much the same manner as its "$Rh_2(dppm)_2$" analogue,[13] by reaction of the trans-dichlorodicarbonyl complex (1) with $Na_2S{\bullet}9H_2O$. The yield of the red solid is somewhat less (62%) than that reported for the dppm counterpart (85-95%) due to significant decomposition of this species. Compound 9 undergoes complete decomposition over a period of several days under a dinitrogen atmosphere to an unidentified brown solid, and is extremely sensitive to oxygen in solution. The $^{31}P\{^1H\}$ NMR spectrum of 9 appears very similar to that of compound 4 and the infrared spectrum shows two carbonyl stretches at 1932 and 1916 cm^{-1}, reminiscent of $[Rh_2(CO)_2(\mu\text{-}S)(dppm)_2]$ ($\nu(CO)$= 1933, 1920 cm^{-1}, Nujol).[13] The $^{13}C\{^1H\}$ NMR spectrum of 9 at room temperature shows a broad singlet at δ 185.2 which resolves into a doublet of triplets (δ 183.8, $^1J_{C\text{-}Rh}$= 69.2 Hz, $^2J_{C\text{-}P}$= 15.2 Hz, CD_2Cl_2 solution) at -93°C. Compound 9 also reacts with CO to give a second order doublet in the $^{31}P\{^1H\}$ NMR spectrum at ambient temperature (δ -21.68, CD_2Cl_2) together with the resonance for the starting material. At the same time the infrared spectrum shows a new intense carbonyl stretch at 1994 cm^{-1} together with the bands due to 9. There is no indication of a bridging carbonyl band other than a very weak band at 1720 cm^{-1}. The carbonyl region of the $^{13}C\{^1H\}$ NMR spectrum at -93°C contains a broad resonance at δ 183.9 (CD_2Cl_2). Based on this information the new species appears to be the tetracarbonyl complex **10**. The additional carbonyl bands expected for a tetracarbonyl species are not observed in the infrared spectrum; presumably being obscured by the broad intense bands of the starting material **9**. The presence of only one resonance in the $^{13}C\{^1H\}$ NMR spectrum suggests rapid CO exchange to be taking place over the four positions. Unlike the related chloro species **8**, compound **10** retains the bridging sulfido group presumably because movement of this dianionic bridging group to a terminal position would result in an unfavorable dipolar compound. The appearance of separate resonances for **9** and **10** in the $^{31}P\{^1H\}$ NMR spectrum at room temperature, indicates that no rapid CO exchange takes place between the two as was observed between the chloro species **4** and **6**. The formation of the tetracarbonyl complex, **10**, is in contrast to the chemistry of both the rhodium and iridium dppm analogues, $[Rh_2(CO)_2(\mu\text{-}S)(dppm)_2]$ [13] and $[Ir_2(CO)_2(\mu\text{-}S)(dppm)_2]$; [19] whereas the rhodium complex did not react with



10

CO, the iridium one did, but to yield a tricarbonyl complex with geometry similar to that of compound **6**. We see no obvious reason for the differences observed in our dmpm-bridged species, except to note that the more basic dmpm ligand would favour CO addition and that this smaller group would tend to allow a higher metal coordination than would dppm.

(b) Reactions with Alkynes. *Trans*-[RhCl(CO)(dmpm)]$_2$ (**1**) reacts with one equivalent of the activated alkynes, dimethyl acetylenedicarboxylate (DMAD) and hexafluoro-2-butyne (HFB), to yield 1:1 adducts of the form [$Rh_2Cl_2(CO)_2$(μ-alkyne)$(dmpm)_2$] (**11**, alkyne= DMAD; **12**, alkyne= HFB). No reaction is observed with the unactivated alkynes phenylacetylene, diphenylacetylene and 2-butyne. Both compounds **11** and **12** are assigned the structure shown below, based on analogies with the alkyne adducts of *trans*-[IrCl(CO)(dppm)]$_2$ [18a] in which the alkyne group bridges the two metals essentially parallel to the metal-metal axis.



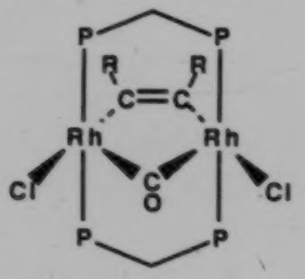
11, R= CO_2Me

12, R= CF_3

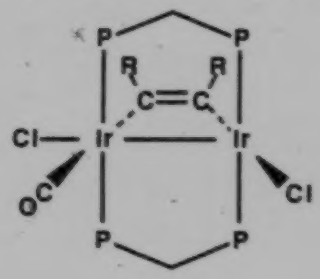
The $^{31}P\{^1H\}$ NMR spectra of both **11** and **12** exhibit complex second order resonances consisting of two pseudodoublets of triplets (Table 2.2). This pattern is typical for an unsymmetrical complex having an

AA'BB'XY spin system by virtue of the chemically inequivalent rhodium atoms. The infrared spectrum of compound **11** (Nujol) displays the carbonyl ligand stretches at 2028 cm^{-1} and 2005 cm^{-1} with additional stretches at 1712 cm^{-1} and 1665 cm^{-1} for the carbonyl groups of the coordinated DMAD group. The infrared spectrum of **12**, on the other hand, displays only one carbonyl stretch at 2030 cm^{-1}. However, based on similarities in the other spectroscopic parameters (IR, NMR) with compound **11** we assume that **12** is also a dicarbonyl species in which the stretches due to both carbonyl ligands appear to be coincident. It is noteworthy that this was exactly the situation observed for $[Ir_2Cl_2(CO)_2(\mu\text{-HFB})(dppm)_2]$.[18a]

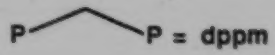
The reaction of $[RhCl(CO)(dmpm)]_2$ (**1**) with alkynes more closely resembles that of *trans*-$[IrCl(CO)(dppm)]_2$[18a] than of *trans*-$[RhCl(CO)(dppm)]_2$.[14f] For the rhodium dppm complex one carbonyl ligand was very labile and the only complex isolated was the unusual species $[Rh_2Cl_2(\mu\text{-CO})(\mu\text{-alkyne})(dppm)_2]$ (alkyne= DMAD, HFB), containing a bridging carbonyl ligand but no accompanying Rh-Rh bond (see structure A). The more basic dmpm ligand apparently imparts enough basicity to the



A

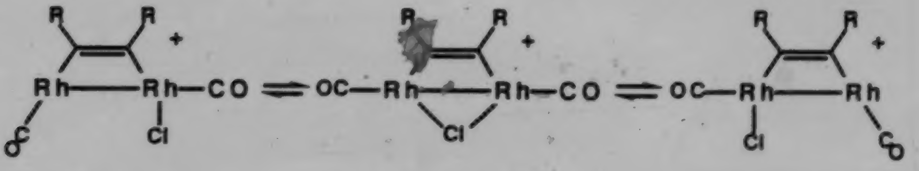


B



rhodium atoms to decrease the lability of this carbonyl group via π back-donation, much as was the case for the "$Ir_2(dppm)_2$" complexes. Upon heating, the iridium species, $[Ir_2Cl_2(CO)_2(\mu\text{-alkyne})(dppm)_2]$, did lose one carbonyl ligand, however, the resulting products had the remaining carbonyl ligand terminally bound with an Ir-Ir bond (structure B).[18a] We were interested in labilizing one of the carbonyl ligands in **11** or **12** to discover which structural type would be adopted by the "$Rh_2(dmpm)_2$" system. Unfortunately attempts to obtain the monocarbonyl products failed; trimethylamine oxide did not remove a carbonyl group and heating under reflux in various solvents resulted in decomposition of the starting material to a number of unidentified products.

The cationic alkyne-bridged complexes, $[Rh_2Cl(CO)_2(\mu\text{-}RC_2R)\text{-}(dmpm)_2][BF_4]$ (**13**, R = CO_2CH_3; **14**, R= CF_3), can be prepared by either chloride ion removal from compounds **11** and **12**, respectively, or by the direct reaction of the cationic A-frame $[Rh_2(CO)_2(\mu\text{-}Cl)(dmpm)_2][BF_4]$ (**4**) with the alkyne molecules DMAD or HFB. These cationic species are assigned the geometry shown below (dmpm groups perpendicular to the plane of the paper are omitted). At room temperature both complexes **13** and **14** display broad resonances in the $^{31}P\{^{1}H\}$ NMR spectrum, suggestive



13, R= CO_2CH_3
14, R= CF_3

of symmetrical species, however, lowering the temperature to -40°C results in the appearance of patterns typical for unsymmetrical species (see Figure 2.3). This temperature dependence suggests a fluxionality, as was observed for the analogous "$Ir_2(dppm)_2$" systems, in which chloride ligand transfer from one metal to the other occurs. Such processes appear to be common in these systems.[14f,28-30]

In the infrared spectra of compound **13**, two bands appear for the terminal carbonyl ligands at 2036 and 2023 cm^{-1} and a broad band for the DMAD carbonyl groups is also present at 1687 cm^{-1}. For compound **14** only one terminal carbonyl band is observed at 2045 cm^{-1}, as was the case for the parent compound **12**. However, the fluxionality of this system and the similarity of its spectroscopic properties to **13** make it clear that it is also a dicarbonyl complex. For all alkyne-bridged complexes the C=C stretches for the cis-dimetallated olefinic moiety are observed near 1560 cm^{-1} (see Table 2.1), and the ^1H NMR parameters (see Table 2.2) are consistent with the species proposed.

In the analogous "$Ir_2(dppm)_2$" chemistry, chloride removal from $[Ir_2Cl_2(CO)_2(\mu\text{-alkyne})(dppm)_2]$ and alkyne addition to $[Ir_2(CO)_2(\mu\text{-Cl})(dppm)_2]^+$ resulted in different isomers, the latter of which slowly rearranged to the more stable one.[18a] In the "$Rh_2(dmpm)_2$" chemistry presented here, only one isomer is observed in these cationic alkyne adducts, that which is analogous to the thermodynamically more stable diiridium species. While it may be that only this isomer is formed, it may also be that alkyne attack at $[Rh_2(CO)_2(\mu\text{-Cl})(dmpm)_2]^+$ yields the unstable isomer, analogous to the iridium system, but subsequent rearrangement to

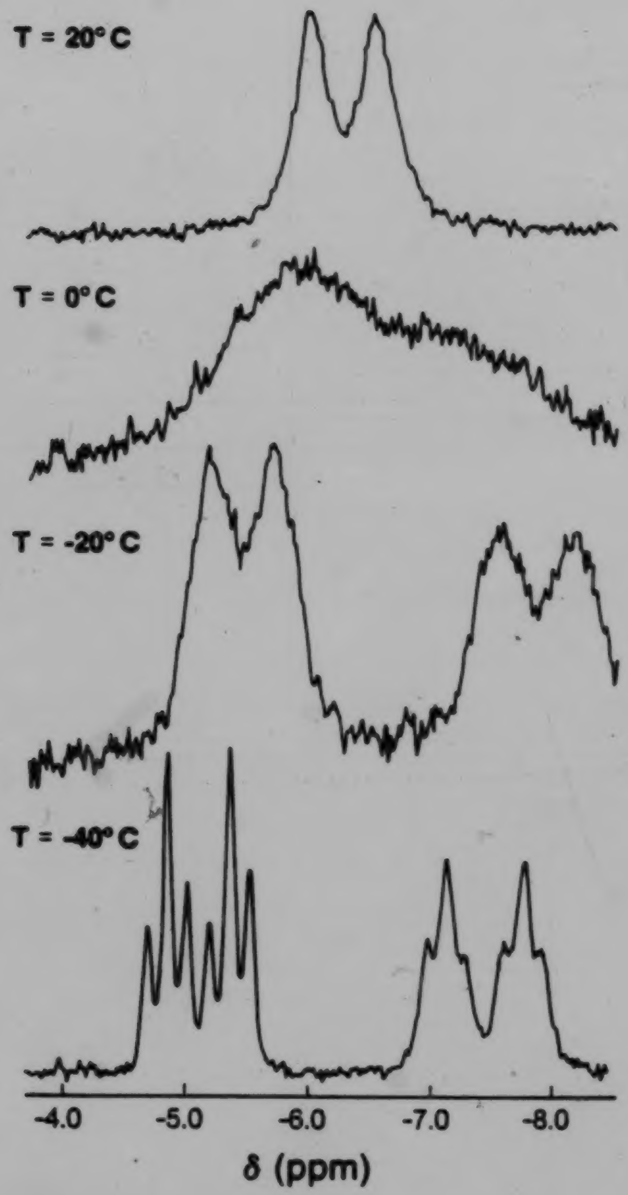


Figure 2.3. The $^{31}P\{^1H\}$ NMR spectrum of $[Rh_2Cl(CO)_2(\mu\text{-}HFB)(dmpm)_2][BF_4]$ (13) between -40° and 20°C.

the more stable one is extremely facile. This presumed rapid isomerization is consistent with the greater lability of the second row transition metals over their third row counterparts, and with the smaller dmpm ligand facilitating such a process, although it must be stressed that our presumption of another isomer being involved is based solely on analogies with the "$Ir_2(dppm)_2$" chemistry.

Conclusions

The series of "$Rh_2(dmpm)_2$" complexes reported is quite analogous, although not identical, to those of rhodium and iridium containing the larger and less basic dppm ligand. Both differences in ligand properties (bulk and basicity) are evident in the observed chemical differences for these complexes. Not surprisingly, the more basic dmpm ligand results in better π donation to carbonyl ligands from the metals such that the chemistry of the "$Rh_2(dmpm)_2$" complexes more closely resembles the dppm analogues of iridium than of rhodium. This is seen most clearly in the alkyne adducts where the dicarbonyl complexes $[M_2Cl_2(CO)_2(\mu\text{-alkyne})\text{-}(diphosphine)_2]$ and $[M_2Cl(CO)_2(\mu\text{-alkyne})(diphosphine)_2]^+$ (M = Rh, diphosphine= dmpm; M = Ir, diphosphine= dppm) are in contrast with the only observed "$Rh_2(dppm)_2$" species, $[Rh_2Cl_2(\mu\text{-CO})(\mu\text{-alkyne})(dppm)_2]$. Similarly the tetracarbonyl species $[Rh_2Cl(CO)_3(\mu\text{-CO})(dmpm)_2]^+$ (**8**) and $[Rh_2(CO)_4(\mu\text{-S})(dmpm)_2]$ (**10**) were obtained with the dmpm group whereas with dppm only the tricarbonyl, $[Rh_2(CO)_2(\mu\text{-Cl})(\mu\text{-CO})(dppm)_2]^+$, and the dicarbonyl, $[Rh_2(CO)_2(\mu\text{-S})(dppm)_2]$, compounds were observed.

The smaller steric bulk of the dmpm group appears to allow more facile ligand rearrangements over the two metals, so the observation of only one isomer of $[Rh_2Cl(CO)_2(\mu\text{-alkyne})(dmpm)_2]^+$ (**13**, alkyne= DMAD; **14**, alkyne= HFB) rather than the two observed with the "$Ir_2(dppm)_2$" system [18a] may be due to facile isomerization. In addition, it may be that the greater lability of $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(dmpm)_2]^+$ (**6**) compared with its dppm analogue is due to more facile rearrangement within the complex.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, anisotropic thermal parameters and hydrogen atom parameters for this and subsequent structures are available from Dr. M. Cowie, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada. T6G 2G2.

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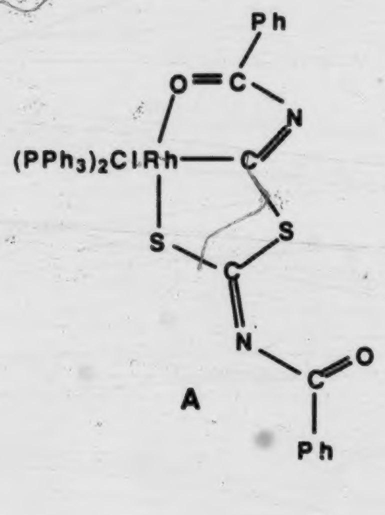
Chapter 3

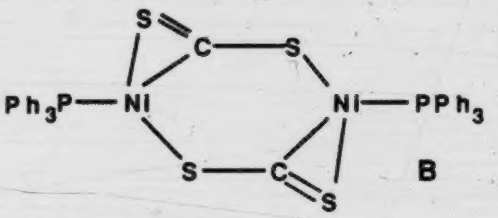
Bis(dimethylphosphino)methane-Bridged Dirhodium Heteroallene Complexes

Introduction

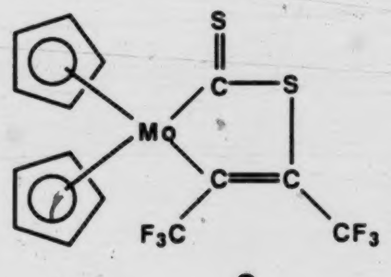
One of the primary goals of organometallic chemistry is the use of transition-metal complexes as templates for the coordination and subsequent combination of organic fragments. In this respect heteroallenes such as isothiocyanates (SCNR) and carbon disulfide (CS_2) have proven quite versatile in the variety of coordination modes they exhibit and the types of combination reactions they undergo at metal centres.[1-4] Representative examples include the formation of condensation products such as **A** [7] (at one or two metal centres),[5-10] η^2-CS_2 bridging complexes,[7a,7b,9,11-15] of type **B**[12] and metallocyclic species [16,17] in which another molecule such as an alkyne has been incorporated into a ring structure, **C**.[17] Considerable attention has also been focused on the



A



B



C

chemistry of CS_2 and other heteroallenes in relation to their possible of use as models for CO_2 activation.[1,2,13]

The cooperative role that more than one metal centre, in multinuclear transition-metal complexes, may play in the coordination and subsequent reaction of heteroallenes has been of particular interest to our group[10] and others.[9,13-15] Since heteroallenes readily coordinate to more than one metal centre it was anticipated that their reaction with "$Rh_2(dmpm)_2$" complexes would provide examples of heteroallene ligand coordination involving both metals. In this respect previous studies undertaken by this group on the reaction of $[Rh_2Cl_2(\mu\text{-}CO)(dppm)_2]$ with CS_2[10a,10b] and a variety of isothiocyanate molecules[10c] yielded bridging 1:1 adducts or 2:1 condensation products. The formation of similar species in the "$Rh_2(dmpm)_2$" system would allow us to extend the comparisons of "$Rh_2(dmpm)_2$" and "$Rh_2(dppm)_2$" chemistry begun in Chapter 2. We were also interested in making use of the electron-rich nature of the metal centres of the "$Rh_2(dmpm)_2$" complexes for the coordination of electrophilic molecules such as C(O)S and CO_2.

In this Chapter the reactions of *trans*-$[RhCl(CO)(dmpm)]_2$ with the heteroallenes $SCNCO_2Et$, CS_2, and C(O)S and the reaction of $[Rh_2(CO)_2(\mu\text{-}Cl)(dmpm)_2][BF_4]$ with CS_2 are discussed and the resulting products compared with the known "$Rh_2(dppm)_2$" analogues.

Experimental

General Comments. Silver tetrafluoroborate ($AgBF_4$) and ethoxycarbonyl isothiocyanate ($SCNCO_2Et$) were purchased from The

Aldrich Chemical Company, carbon disulfide (CS_2) from The McArthur Chemical Company and sodium sulfide hydrate ($Na_2S\bullet9H_2O$) from The J. T. Baker Chemical Company. Carbon monoxide (C. P. grade) and carbonyl sulfide (C(O)S) were purchased from Matheson and ^{13}CO (99%) from Isotec Inc. These and all other reagent-grade chemicals were used as received. The compounds *trans*-$[RhCl(CO)(dmpm)]_2$, $[Rh_2(CO)_2(\mu\text{-}Cl)(dmpm)_2][BF_4]$ and $[RhCl_2(CO)(dmpm)]_2$ were prepared by the procedures reported in Chapter 2. The $^{31}P\{^1H\}$ NMR spectra of samples involving carbonyl sulfide were recorded in CH_2Cl_2 solution on a Bruker WP-200 spectrometer at 81 MHz using an internal deuterium lock ($(CD_3)_2CO$); all others were recorded on a Bruker AM-400 spectrometer at 161 MHz in CD_2Cl_2 solution. In all cases phosphorus chemical shifts were measured relative to 85% H_3PO_4. Infrared spectra of samples involving carbonyl sulfide were recorded on a Perkin-Elmer model 883 infrared spectrometer in CH_2Cl_2 solution in KCl cells. All others were recorded on a Nicolet 7199 Fourier transform infrared spectrometer with the use of nujol mulls on KBr plates or in CH_2Cl_2 solution in KCl cells. All ^1H NMR spectra were recorded at 400 MHz on a Bruker AM-400 spectrometer.

Preparation of Compounds. (a) $[Rh_2Cl_2(CO)(\mu\text{-}SCNCO_2Et)(dmpm)_2]$ (1). One equiv of ethoxycarbonyl isothiocyanate (9.8 μL, 0.083 mmol) was added to a solution of *trans*-$[RhCl(CO)(dmpm)]_2$ (50 mg, 0.083 mmol) dissolved in CH_2Cl_2 (6 mL). After stirring for 2 h, diethyl ether (20 mL) was added and the solution cooled to 0°C. The solvents were removed by cannula under positive dinitrogen pressure, the orange solid was washed repeatedly with diethyl ether and then dried under dinitrogen. The orange product was isolated in 77% yield (45 mg). Anal. Calcd for $C_{15}Cl_2H_{33}NO_3P_4SRh_2$: C, 25.4%; Cl, 10.0%; H, 4.7%; N, 2.0%; S, 4.5%. Found: C, 25.4%; Cl, 10.6%; H, 4.6%; N, 2.0%; S, 4.7%.

(b) [$Rh_2Cl_2(CO)\{\mu$-$SCNC(S)N(CO_2Et)_2\}(dmpm)_2$] (2). A 100 mg sample of *trans*-[RhCl(CO)(dmpm)]$_2$ (0.165 mmol) was dissolved in CH_2Cl_2 (10 mL), 2 equiv of ethoxycarbonyl isothiocyanate (39 µL, 0.33 mmol) was added and the mixture stirred for 1 h. Diethyl ether (25 mL) was added to the orange-yellow solution and the mixture cooled to 0°C. Removal of the solvents by cannula under positive dinitrogen pressure, subsequent washing of the solid with diethyl ether and drying under vacuum afforded the orange-yellow product in essentially quantitative yield. Anal. Calcd for $C_{19}Cl_2H_{38}N_2O_5P_4S_2Rh_2$: C, 27.2%; Cl, 8.4%; H, 4.6%; N, 3.3%; S, 7.6%. Found: C, 27.6%; Cl, 9.6%; H, 4.7%; N, 3.2%; S, 7.5%.

(c) [$Rh_2Cl_2(CO)(C_2S_4)(dmpm)_2$]·1/2 CH_2Cl_2 (3). Carbon disulfide (0.15 mL, 2.50 mmol) was added to a solution of *trans*-[RhCl(CO)(dmpm)]$_2$ (75 mg, 0.124 mmol) dissolved on CH_2Cl_2 (8 mL) . Stirring for 10 min resulted in the precipitation of an orange solid. After stirring for a total of 40 min, diethyl ether (25 mL) was added and the mixture cooled to 0°C. The solvents were removed by cannula under positive dinitrogen pressure, the orange solid was washed twice with 10 mL portions of THF and then dried under vacuum. Compound **3** was isolated as an orange powder in 68% yield (65 mg). The presence of CH_2Cl_2 solvate was confirmed by ^1H NMR spectroscopy in THF-d_8. Anal. Calcd for $C_{13.5}Cl_3H_{29}OP_4S_4Rh_2$: C, 21.0%; Cl, 13.8%; H, 3.8%. Found: C, 21.1%; Cl, 13.7%; H, 3.6%.

(d) [$Rh_2Cl(CO)(C_2S_4)(dmpm)_2$][$BF_4$] (4). An excess of carbon disulfide

(20 µL, 0.332 mmol) was added to a solution of $[Rh_2(CO)_2(\mu\text{-}Cl)(dmpm)_2][BF_4]$ (54 mg, 0.083 mmol based on 100% conversion of 50 mg of *trans*-$[RhCl(CO)(dmpm)]_2$) in CH_2Cl_2 (10 mL) resulting in the immediate formation of a brown-red precipitate. After stirring for 15 min the solvent was removed by cannula under positive dinitrogen pressure, the solid was washed repeatedly with diethyl ether and then dried under vacuum. Compound **4** was isolated as a brown-red solid in 68% yield (44 mg). Anal. Calcd for $BC_{13}ClF_4H_{28}OP_4S_4Rh_2$: C, 20.0%; Cl, 4.5%; H, 3.6%; S, 16.4%. Found: C, 20.1%; Cl, 4.6%; H, 3.7%; S, 15.1%.

Reaction of *trans*-$[RhCl(CO)(dmpm)]_2$ with C(O)S. A static atmosphere of carbonyl sulfide was placed over a solution of *trans*-$[RhCl(CO)(dmpm)]_2$ (100 mg, 0.165 mmol) dissolved in CH_2Cl_2 (10 mL). Upon stirring for 16 h the solution colour changed from red-orange to dark orange. The volume of the solvent was reduced to ca. 4 mL by passing a stream of dinitrogen over the solution. All reaction products were characterized by $^{31}P\{^1H\}$ NMR and solution infrared spectroscopy obtained on the reaction mixture under dinitrogen or carbon monoxide.

Results and Discussion

The addition of 1 or 2 equiv of ethoxycarbonyl isothiocyanate ($SCNCO_2Et$) to a solution of *trans*-$[RhCl(CO)(dmpm)]_2$ in CH_2Cl_2 yields the air-sensitive 1:1 adduct $[Rh_2Cl_2(CO)\{\mu\text{-}SCNCO_2Et\}(dmpm)_2]$ (**1**) or the 2:1 adduct $[Rh_2Cl_2(CO)\{\mu\text{-}SCNC(S)N(CO_2Et)_2\}(dmpm)_2]$ (**2**), respectively. These results parallel those of the closely related "$Rh_2(dppm)_2$" system in which the reaction of $[Rh_2Cl_2(\mu\text{-}CO)(dppm)_2]$ with a variety of isothiocyanates (methyl-, phenyl-, benzoyl- and ethoxycarbonyl isothiocyanate) yielded analogous 1:1 and 2:1 complexes.[10c]

Complementary to this previous study, a preliminary X-ray structure determination of compound **1** has confirmed the proposed mode of isothiocyanate coordination in such complexes. The basic connectivity is clearly established (Figure 3.1) with the isothiocyanate ligand bound through carbon to one metal centre and through sulfur to the other in a bridged manner, forming a four-membered dimetallacyclic ring. A third interaction between the oxygen atom of the organic carbonyl moiety and a rhodium atom is also apparent, forming a five-membered metallacyclic ring. This latter type of coordination of the carbonyl group has been observed for benzoyl- and ethoxycarbonyl isothiocyanate ligands in mononuclear rhodium complexes.[6,7] Due to disorder of the isothiocyanate ligand and of the dmpm methyl groups, and due to decomposition of the crystals, the structure has not been sufficiently refined to warrant a detailed structural discussion; nevertheless the ligand coordination mode is obvious. Subsequent attempts to grow better quality crystals, suitable for completion of the determination, have not succeeded.

The infrared spectrum of compound **1** reveals a single terminal carbonyl stretch at 2023 cm^{-1} (Nujol, see Table 3.1) but no band attributable to the organic carbonyl moiety. The absence of this latter band is consistent with the coordination of this group at one Rh centre. This conclusion was also reached for the analogous dppm-bridged species $[Rh_2Cl_2(CO)$-$(\mu$-$SCNCO_2Et)(dppm)_2]$.[10c] In the solution infrared spectrum of compound **1**, however, a weak-intensity band appears at 1751 cm^{-1}. The frequency of

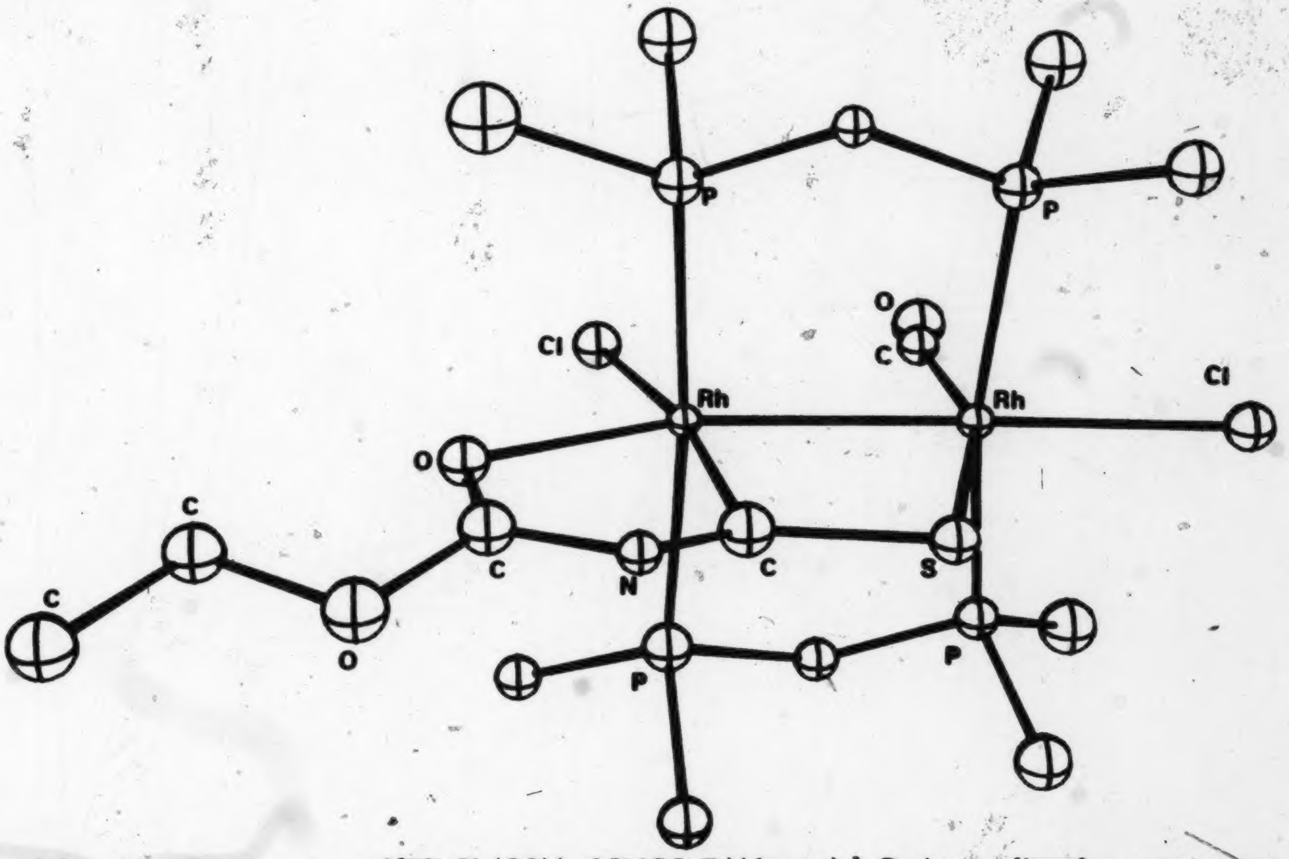


Figure 3.1. A perspective view of [$Rh_2Cl_2(CO)(\mu\text{-}SCNCO_2Et)(dmpm)_2$]. Owing to disorder, some atoms are shown with arbitrary sized thermal ellipsoids.

Table 3.1. Infrared Spectroscopic Data for the Compounds in Chapter 3.[a]

no.	compound	Nujol, cm^{-1}		CH_2Cl_2 solution, cm^{-1}	
		v(CO)	others	v(CO)	others
1	$[Rh_2Cl_2(CO)(\mu\text{-}SCNCO_2Et)(dmpm)_2]$	2023(m)	1508(w)[b]	2033(s), 1751(m)[c]	1515(m)[b]
2	$[Rh_2Cl_2(CO)\{\mu\text{-}SCNC(S)N(CO_2Et)_2\}(dmpm)_2]$	2013(vs)	1581(m),[b] 1514(m)[b]	2020(vs)	1580(m),[b] 506(m)[b]
		1776(m),[c]		1775(s),[c]	
		1712(m)[c]		1712(m)[c]	
3	$[Rh_2Cl_2(CO)(C_2S_4)(dmpm)_2]\cdot 1/2CH_2Cl_2$	2015(s)	1047(w),[d] 978(w)[d]	2020(s)	1046(m),[d] 980(m)[d]
4	$[Rh_2Cl(CO)(C_2S_4)(dmpm)_2][BF_4]$	2034(m)	1024(m),[d] 969(m)[d]		
5	$[Rh_2Cl_2(CO)_2(\mu\text{-}C(O)S)(dmpm)_2]$			2044(s), 1993(m)	
				1680(w)[e]	
6	$[Rh_2Cl_2(CO)_2(\mu\text{-}S)(\mu\text{-}CO)(dmpm)_2]$			2064(s), 2057(m),	
				1698(m)	
7	$[Rh_2Cl_2(CO)_2(\mu\text{-}S)(dmpm)_2]$	2013(m)		2013(s)	

[a] Abbreviations used: vs, very strong; s, strong; m, medium; w, weak. [b] v(CS) and v(CN). [c] v(CO) of CO_2Et. [d] v(CS). [e] v(CO) of C(O)S.

this new band is characteristic of an uncoordinated ethoxycarbonyl fragment. Thus, it appears that in solution the oxygen atom of the organic carbonyl group dissociates from the rhodium atom, resulting in the new band. This process is illustrated by figures **a** and **b** in Scheme 3.1. The low intensity of the new band relative to that of the metal-carbonyl stretch suggests that the dissociation isn't complete and both forms are likely in equilibrium in solution. An additional band at 1508 cm^{-1} in the infrared spectrum of **1** is assigned to the vibrations involving interaction between C=S and C-N stretching (range 1563-700 cm^{-1} in organic compounds)[18] of the isothiocyanate ligand.

The possibility that the new band is due to the formation of a bridging metal carbonyl species has been discounted on the basis of solution infrared studies. When complex **1** is exposed to ^{13}CO, a band at 1988 cm^{-1} grows in, indicating that an exchange between ^{13}CO and the terminal metal-carbonyl ligand takes place, but there is no change in the band at 1751 cm^{-1} and no evidence of a bridging carbonyl ligand. In contrast, the "$Rh_2(dppm)_2$" analogue was found to have a bridging carbonyl ligand in the solid state which transformed to terminally bound CO in solution.[10c]

The $^{31}P\{^1H\}$ NMR spectrum of compound **1** consists of a complex multiplet at δ -2.86 (see Table 3.2). Due to the complex nature of the resonance, we were unable to determine whether a second resonance for the uncoordinated ethoxycarbonyl species was also present. In the ^1H NMR spectrum we see evidence of the coordinated and uncoordinated ethoxycarbonyl fragments with the appearance of two sets of resonances.

Scheme 3.1

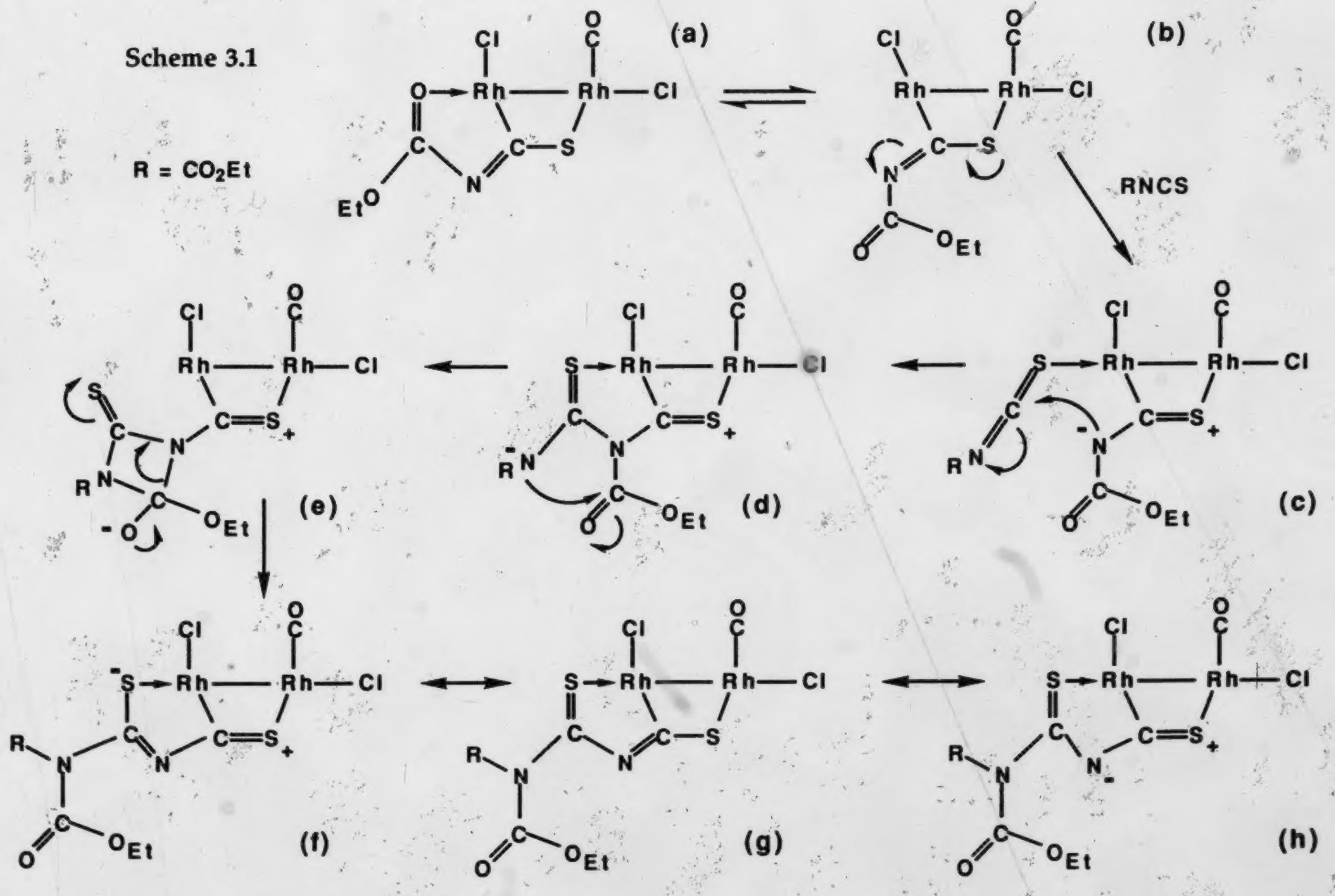


Table 3.2. **NMR Spectroscopic Data for the Compounds in Chapter 3.**[a,b]

compound	$\delta(^{31}P(^{1}H))^{c}$	$\delta(^{1}H)$		
		$P\text{-}CH_3$	$\text{-}CH_2\text{-}$	others
1	-2.86(m)	1.84(t, 3 H, J=3 Hz), 1.78(t, 3 H, J=4 Hz), 1.76(t, 3 H, J=4 Hz), 1.71(t, 3 H, J=3 Hz), 1.67(t, 3 H, J=3 Hz), 1.37(t, 6 H, J=3 Hz), 1.18(t, 3 H, J=3 Hz)	2.79(m, 2H) 2.52(m, 2H)	4.29, 4.28(qr, 2 H, J=7 Hz)[d] 1.34, 1.32(t, 3 H, J=7 Hz)[e]
2	-0.91(dt, 63, 29 Hz), -3.44(dt, 96, 27 Hz)	1.85(t, 6 H, J=3 Hz), 1.69(m, 12 H), 1.28(t, 6 H, J=2 Hz)	2.81(m, 4 H)	4.47, 4.18(qr, 2 H, J=7 Hz)[d] 1.38(t, 3 H, J=7 Hz),[e] 1.31(m, 3H)[e]
3	-1.64(dt, 88, 24 Hz), -5.36(dt, 97, 24 Hz)	1.86(t, 6 H, J=3 Hz), 1.73(t, 6 H, J=4 Hz), 1.66(t, 6 H, J=4 Hz), 1.32(t, 6 H, J=3 Hz)	2.81(m, 4 H)	
5	-1.01(dt, 88, 25 Hz), -4.80(dt, 97, 25 Hz)			
6	1.12(d, 116 Hz)			
7	-5.23(d, 87 Hz)			

---

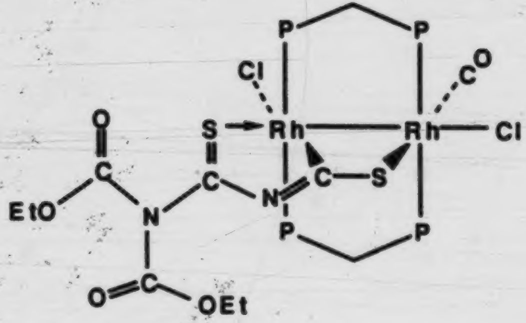
[a] Ambient temperature in CD_2Cl_2 except compounds 5, 6, and 7 (CH_2Cl_2). [b] Abbreviations used: d, doublet; t, triplet; qr, quartet; dt, doublet of triplets; m, multiplet. [c] Vs 85% H_3PO_4, numbers in parentheses represent the separation in hertz between the major peaks in the second-order spectrum of the complex. [d] $\text{-}OCH_2\text{-}$. [e] $C\text{-}CH_3$.

The methylene protons appear as two overlapping resonances at δ 4.29 and δ 4.28 with a relative integrated intensity of approximately 1:2. Both are quartets due to three-bond coupling to the methyl protons ($^3J_{H\text{-}H}$= 7 Hz), which themselves appear as triplets at δ 1.34 and δ 1.32 with relative integrated intensities of 2:1. In considering the intensities of these resonances, those at δ 4.28 and δ 1.34 have been assigned to one ethoxycarbonyl group and those at δ 4.29 and δ 1.32 to the other. Presumably the lower intensity set of resonances is due to the uncoordinated ethoxycarbonyl group of structure **b** in Scheme 3.1. This assignment is consistent with the solution infrared data which, on the basis of the weak intensity CO band (1751 cm^{-1}), indicates structure **b** to be present in lower concentration than **a**. The remaining resonances in the ^1H NMR spectrum are attributed to the protons of the dmpm ligands, (δ (PCH_2) 2.79 and 2.52; δ (PCH_3), a series of triplets ranging from δ 1.84 to δ 1.18, see Table 3.2).

The identification of species **b** in Scheme 3.1, in which the ethoxycarbonyl moiety is not coordinated at one metal, is significant since this species represents a key intermediate in the mechanism by which the second isothiocyanate molecule is incorporated into complexes such as **1**. This mechanism, mentioned earlier, was first presented in detail for the analogous "$Rh_2(dppm)_2$" system [10c] and has been reproduced in Scheme 3.1. In solution, dissociation of the ethoxycarbonyl group from the rhodium centre provides a vacant site for the coordination of the second isothiocyanate molecule through sulfur. Upon initial coordination of the second SCNR group, nucleophilic attack by the nitrogen at the carbon atom of the new ligand (**c**) and subsequent attack of the second nitrogen at the carbonyl carbon (**d**) results in C-N bond formation (**e**). Dissociation of sulfur from the metal atom at this point (**e**) may take place in order to help reduce the strain in the four-membered ring. The original C-N bond is then broken and the ethoxycarbonyl group undergoes a 1, 3 shift to provide the final complex (**2**), which can be described by the resonance structures **f**, **g** and **h**.

The fact that no further condensation of isothiocyanate is observed in either of the "$Rh_2(dmpm)_2$" or "$Rh_2(dppm)_2$" systems is rationalized in terms of the strong interaction of the relatively soft sulfur atom in **f** with rhodium compared to the weaker interaction of rhodium with the harder oxygen atom in **a**.[19] Failure of the thiocarbonyl moiety to dissociate leaves the rhodium centre coordinatively saturated so there is no available site for the coordination of a third SCNR group. The nitrogen atom in the final 2:1 adduct is also expected to be a poorer nucleophile than it was in the 1:1 adduct, owing to steric inhibition by the two ethoxycarbonyl groups. The effective nucleophilicity of nitrogen should also be affected by charge delocalization over the three structures **f**, **g** and **h** (Scheme 3.1(c)).

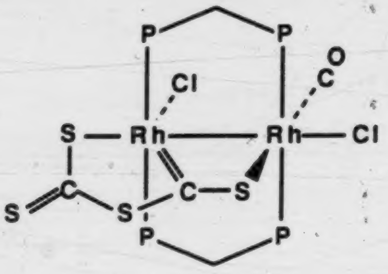
The characterization of the product of the isothiocyanate condensation, $[Rh_2Cl_2(CO)\{\mu\text{-}SCNC(S)N(CO_2Et)_2\}(dmpm)_2]$ (**2**), is based primarily on the similarities of the observed spectroscopic data with that of the dppm analogue [10c] and the agreement of the elemental analysis results with such a formulation. The $^{31}P\{^1H\}$ NMR spectrum of this compound exhibits the familiar two sets of doublets of triplet resonances (δ -0.91 and δ -3.44) which are typical of an AA'BB'XY spin system and an



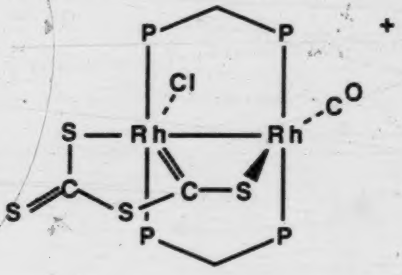
2

unsymmetrical "Rh_2(diphosphine)$_2$" complex (see Chapters 2 and 4 for pictorial examples of such spectra). The infrared spectrum of compound 2 contains a single intense band at 2013 cm^{-1} attributed to the terminally bound carbonyl ligand and two lower frequency bands (ν(CO) = 1776 and 1712 cm^{-1}) which are assigned to the organic carbonyl fragments of the condensed isothiocyanate ligand. As expected, the metal-carbonyl stretching frequency of compound 2 is lower than the corresponding band of the dppm analogue (ν(CO)= 2026 cm^{-1}),[10c] a consequence of the basicity of the dmpm ligands. Additional infrared bands due to ν(SCN) vibrations are present at 1581 and 1514 cm^{-1}. In the ^1H NMR spectrum of complex 2 the methylene protons of the two ethoxycarbonyl groups show up clearly as a pair of resonances at δ 4.47 and δ 4.18. Three-bond coupling to the methyl protons is on the order of 7 Hz. The methyl protons appear as one triplet (δ 1.38) and a multiplet (δ 1.31). The remainder of the spectrum consists of resonances due to the dmpm protons (δ(PCH_3)= 1.85t(6H), 1.69t(12H), 1.28t(6H); δ(CH_2)= 2.81m(4H)).

The compounds, *trans*-[RhCl(CO)(dmpm)]$_2$ and [$Rh_2(CO)_2$(μ-Cl)-(dmpm)$_2$][BF_4] react with excess CS_2 in CH_2Cl_2 to yield the condensation products $[Rh_2Cl_2(CO)(C_2S_4)(dmpm)_2]\cdot 1/2\ CH_2Cl_2$ (**3**) and $[Rh_2Cl(CO)(C_2S_4)(dmpm)_2][BF_4]$ (**4**), respectively. The formulation of complex **3** is assigned on the basis of its elemental analysis and the similarities of its spectroscopic data (Tables 3.1 and 3.2) with those of the closely related $[Rh_2Cl_2(CO)(C_2S_4)(dppm)_2]$.[10a,b] The insolubility of the cationic



3

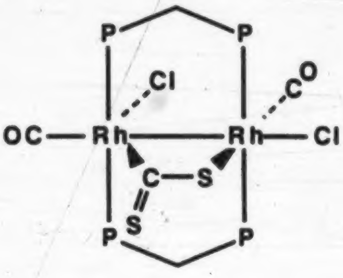


4

species **4** in common organic solvents has limited its subsequent characterization to elemental analysis and the solid-state infrared spectrum but it is also presumed to have the same type of structure with the exception of one less chloride ligand coordinated to a rhodium centre. In both **3** and **4**, as had been first proposed for the neutral dppm analogue, the C_2S_4 ligand can be described as a $C_2S_4^{-2}$ carbene with the sulfur and carbene atoms both donating two electrons to Rh(II) centres.[10a,10b] The geometry of these compounds is also closely related to that of the isothiocyanate product **2**.

The pathway for coordination and subsequent condensation of CS_2 is modeled after the mechanism of isothiocyanate condensation on $[Rh_2Cl_2(\mu\text{-}CO)(dppm)_2]$, presented earlier (Scheme 3.1).[10c] The addition of 1

CS_2 molecule most likely involves the formation of a bridged η^2-CS_2 species, D, which is similar in form to the complexes $[Pt_2(\eta^2\text{-}CS_2)(PPh_3)_4]$ [20] and $[MM'Cl_2(\eta^2\text{-}CS_2)(dppm)_2]$, [M= M'= Pt; M= M'= Pd; M= Pt, M'= Pd).[21-24] Coordination of a second CS_2 molecule through sulfur at the site left



D

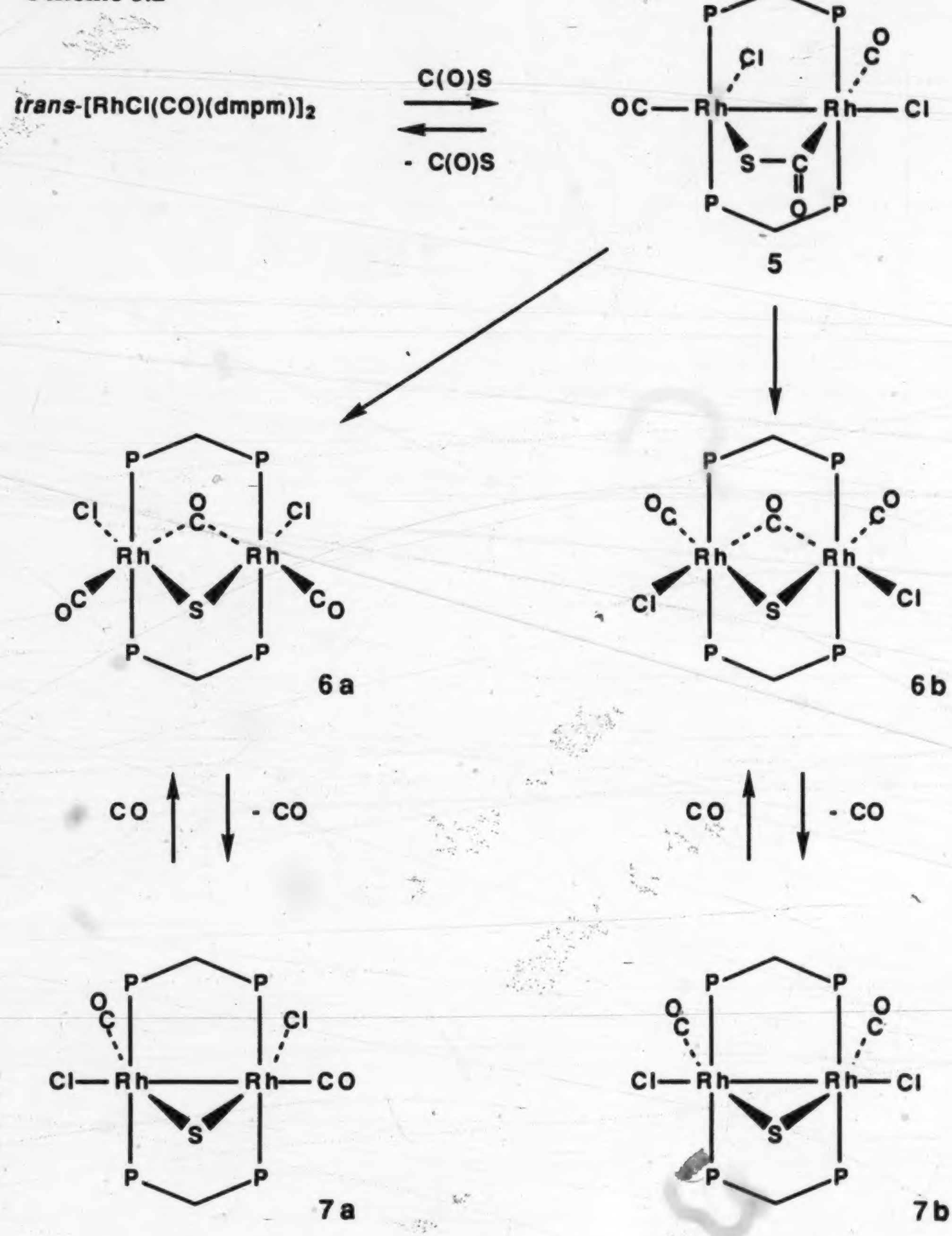
vacant by CO dissociation is presumably followed by nucleophilic attack at the electrophilic carbon atom by the uncoordinated sulfur atom of the first CS_2 ligand. The nucleophilicity of the uncoordinated sulfur atom is well known from the reaction of mononuclear CS_2 complexes with reagents such as alkyl halides.[25-27] The result is the formation of a C-S bond in much the same manner that the C-N bond is formed in parts **c** and **d** of Scheme 3.1. Attempts to prepare the initial 1:1 adducts by adding one equiv of CS_2 to either *trans*-$[RhCl(CO)(dmpm)]_2$ or $[Rh_2(CO)_2(\mu\text{-}Cl)\text{-}(dmpm)_2][BF_2]$ yields only the starting materials and a small amount of the respective 2:1 products **3** and **4**.

The $^{31}P\{^1H\}$ NMR spectrum of **3** contains resonances at δ -1.64 and δ -5.36, each one a doublet of virtual triplets, consistent with the proposed unsymmetrical geometry and a second-order AA'BB'XY spin system. The ^1H NMR spectrum reveals a set of four methyl proton resonances (δ 1.86, 1.73, 1.66, 1.32) all appearing as virtual triplets due to coupling with two chemically equivalent phosphorus atoms. Each triplet represents two methyl groups which are on the same side of the Rh_2P_4 plane and are on the two phosphorus atoms bound to the same rhodium atom.

Complexes **3** and **4** both exhibit a single terminal CO stretch (ν(CO)= 2015 and 2034 cm^{-1}, respectively) and two CS stretches (ν(CS)= 1047, 978 cm^{-1} and 1024, 969 cm^{-1}, respectively) in the solid state infrared spectrum. The low CO and CS stretches of **3** compared to those of its dppm analogue ($[Rh_2Cl_2(CO)(C_2S_4)(dppm)_2]$, ν(CO)= 2040(sh), 2020(m) cm^{-1} , ν(CS)= 1050 s, 995(sh), 980(vs) cm^{-1}) are consistent with the greater basicity of the dmpm ligands. The electronic difference between dmpm and dppm is also reflected in the ability of the starting materials to react with and bind CS_2. In the dmpm system, the reaction of CS_2 with *trans*-$[RhCl(CO)(dmpm)]_2$ and $[Rh_2(CO)_2(\mu\text{-}Cl)(dmpm)_2][BF_4]$ is immediate and irreversible, indicating a strong interaction of the C_2S_4 moiety with the rhodium centres. In contrast, a vast excess of CS_2 is required for a reaction to occur with *trans*-$[RhCl(CO)(dppm)]_2$ and the product, $[Rh_2Cl_2(CO)(C_2S_4)(dppm)_2]$, loses C_2S_4 in the absence of CS_2. The A-frame species $[Rh_2(CO)_2(\mu\text{-}Cl)(dppm)_2][BF_4]$ does not react at all with CS_2.[10a,10b]

The outcome of the reaction of C(O)S with *trans*-$[RhCl(CO)(dmpm)]_2$ is quite different from that of CS_2. The results of this investigation have been summarized in Scheme 3.2, however, it should be noted that none of the products illustrated have been successfully isolated in pure form. The relative amounts of species obtained was variable and the reaction itself was often not complete even when carried

Scheme 3.2



out over several days. Through correlation of $^{31}P\{^1H\}$ NMR and infrared spectroscopic data, obtained on the reaction mixture, we have been able to determine the form of the products.

The first step in the reaction is proposed to involve the coordination of a C(O)S molecule in a bridged fashion between the two metal centres in much the same manner as CS_2 in the complexes discussed earlier [20-24] (species D), to yield $[Rh_2Cl_2(CO)_2(\eta^2\text{-}C(O)S)(dmpm)_2]$ (5). The presence of similar intermediates have been suggested in the reactions of the multinuclear complexes $[Pt_2(dppm)_3]$ [28] and $[Pt_3(\mu_3\text{-}CO)(dppm)_3]^{2+}$ [29] with C(O)S. Coordination through carbon and sulfur rather than carbon and oxygen is assumed on the basis of hard-soft acid-base theory whereby the softer sulfur atom should show a greater tendency than oxygen to complex to the soft rhodium centre.[19] In support of this assumption, we note that all previously characterized η^2-C(O)S complexes (all mononuclear) have been formulated with this same type of coordination.[30-31] Calculations carried out on the model mononuclear systems of $[Fe(CO)(PH_3)_2(\eta^2\text{-}C(O)S)]$ have shown that η^2-C-S coordination is preferred, largely because of increased π-backdonation from the metal to the π^* orbital of the C(O)S ligand when in this configuration.[32] Calculations made by Mealli, Hoffmann and Stockis have also indicated that COS adducts should prefer η^2-C-S over η^2-C-O coordination.[33]

It is evident from the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture that only one unsymmetrical complex is present and we assign the resonances due to this species (two sets of doublets of triplets at δ -1.01 and δ -4.80) to that of $[Rh_2Cl_2(CO)_2(\eta^2\text{-}C(O)S)(dmpm)_2]$ (5). Bands in the infrared spectrum at 2004 cm^{-1} and 1993 cm^{-1} are attributed to the metal-carbonyl stretches and a third band at 1680 cm^{-1} to the carbonyl moiety of C(O)S. We have found no literature values corresponding to the carbonyl vibration of η^2- coordinated C(O)S groups in binuclear species. As a point of reference, however, the frequency observed for compound **5** is somewhat lower than those reported for mononuclear complexes ([IrCl(CO)$_2$-(η^2-C(O)S)(PMe$_3$)$_2$],[31b] ν(COS)= 1730 cm^{-1}; [Pt(η^2-C(O)S)(PPh$_3$)$_2$],[31d] ν(COS)= 1730 cm^{-1}; [Pd(η^2-C(O)S)(PPh$_3$)$_2$],[31d] ν(COS)= 1740 cm^{-1}; [RhCl(PCy$_3$)$_2$-(C(O)S)],[30] ν(COS)= 1762 cm^{-1}, Cy= cyclohexyl). Upon flushing the solution of compound **5** with N$_2$, all three infrared bands noted above, as well as the ^{31}P{^{1}H} NMR resonances due to this unsymmetrical intermediate, disappear. This coincides with the appearance of spectroscopic features attributed to the starting material *trans*-[RhCl(CO)(dmpm)]$_2$ (IR, ν(CO)= 1965 cm^{-1}; ^{31}P{^{1}H} NMR, δ -3.56). The ease with which C(O)S is removed from the complex is consistent with its generally poorer electron affinity (relative to CS$_2$) [2] and subsequent weaker interaction with metal complexes.

The second compound proposed in Scheme 3.2 is the tricarbonyl species [Rh$_2$Cl$_2$(CO)$_2$(μ-CO)(μ-S)(dmpm)$_2$] (**6**) which results from the disproportionation of the η^2-C(O)S ligand in **5**. Cleavage of the C-S bond predominates in M-C(O)S chemistry [2,31b] and the formation of a bridging sulfide species is consistent with the type of complexes prepared in several platinum systems [28,29,34] and shown in equations 3.1 to 3.3. This general behaviour has been attributed to the relatively weak C-S bond and the affinity of the metals involved for sulfur, as well as the thermodynamic

$$[Pt_2(dppm)_3] \xrightarrow{C(O)S} [Pt_2(\mu\text{-}S)(\eta^1\text{-}dppm)_2(dppm)] + CO \tag{3.1}$$

$$[Pt_3(\mu_3\text{-}CO)(dppm)_3]^{2+} \xrightarrow{C(O)S} [Pt_3(CO)(\mu_3\text{-}S)(dppm)_3]^{2+} + CO \tag{3.2}$$

$$2\ [Pt(\eta^2\text{-}COS)(PPh_3)_2] \xrightarrow{\Delta} [Pt_2(CO)(\mu\text{-}S)(PPh_3)_3] + C(O)S + PPh_3 \tag{3.3}$$

favourability of forming a stable CO molecule. In general, binuclear η^2-C(O)S complexes are quite elusive. In all examples where at least two metal centres are present in the complex or where a second mononuclear compound is introduced into the system, the C(O)S ligand has been found to fragment.[28,29,34]

As shown in Scheme 3.2 the newly created CO ligand remains coordinated to one of the metal centres to give a tricarbonyl product, **6** (**a** or **b**). Consistent with this formulation, three carbonyl stretches appear in the infrared spectrum, two at 2064 and 2057 cm^{-1} which are characteristic of terminal CO and a third at 1698 cm^{-1} which is typical of a bridging CO in a complex without a metal-metal bond.[35-37] The assigned $^{31}P\{^1H\}$ NMR resonance (δ 1.12, a second order doublet) is reminiscent of a symmetrical compound of the form shown in the Scheme as **6a** or **6b**. The configuration of **6b** appears unlikely if you consider that concerted C-S bond cleavage in compound **5** would result in a species in which a carbonyl ligand and a bridging sulfide ligand are adjacent. Nonetheless, it cannot be ruled out and we favour this configuration over that of **6a** since loss of CO results in a complex which is consistent with the configuration of **7b** rather than **7a**. The relative ease with which the third CO ligand can be removed from compound **6** or re-introduced to complex **7** suggests that the disproportionation of C(O)S in complex **5** could just as likely involve the dissociation of CO followed by its re-coordination in the appropriate position. Thus either **6a** or **6b** are possible from the proposed geometry of compound **5**.

The subsequent loss of CO from compound **6** yields a symmetrical dicarbonyl species $[Rh_2Cl_2(CO)_2(\mu\text{-}S)(dmpm)_2]$ (**7**) ($^{31}P\{^1H\}$ NMR ; δ -5.23, a second order doublet; IR, ν(CO) = 2013 cm^{-1}). Terminal CO loss is assumed on the basis of Mague's investigations of the related species $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(dppm)_2]^+$.[38] Removal of CO from **6a** would result in an unsymmetrical compound, **7a**, and a completely different $^{31}P\{^1H\}$ NMR pattern. On the other hand removal of CO from **6b** should provide a symmetrical species, **7b**, consistent with the spectroscopic data. This proposal is made under the assumption that only simple rearrangement of the ligands in the products is possible and that no more than one CO ligand dissociates at any given time. Adding CO to the solution quickly reverses the process and the tricarbonyl species **6** is observed again.

Complex **7** has been prepared independently from the reaction of $[RhCl_2(CO)(dmpm)]_2$ with 1 equiv of $Na_2S{\cdot}9H_2O$ in CH_2Cl_2, and the tricarbonyl species $[Rh_2Cl_2(CO)_2(\mu\text{-}CO)(\mu\text{-}S)(dmpm)_2]$ (**6**) is prepared by passing CO through the reaction solution. Regrettably the reaction of $[RhCl_2(CO)(dmpm)]_2$ with 1 equiv of $Na_2S{\cdot}9H_2O$ is incomplete and does not represent a viable route for the synthesis of either compound **7** or **6** at this time. The addition of excess $Na_2S \cdot 9H_2O$ yields a number of new, as yet uncharacterized, species.

Although we have encountered some difficulty in characterizing the products of the C(O)S reaction the results as presented above are consistent with the findings of others regarding the fragmentation of C(O)S and the form of the products.[28,29,34] Given that *trans*-$[RhCl(CO)(dmpm)]_2$ coordinates C(O)S very weakly and only reacts with it over an extended period of time, it was not surprising that no reaction was observed between *trans*-$[RhCl(CO)(dmpm)]_2$ and CO_2 under the mild conditions used (CH_2Cl_2 solution of *trans*-$[RhCl(CO)(dmpm)]_2$ under 1 atmosphere of CO_2 for 5 days). As a comparison, the related but more electron-rich complex $[Ir_2(CO)_3(dmpm)_2]$ was found to react with CO_2 (yielding the complexes $[Ir(CO)_2(dmpm)]_2$ and $[Ir_2(CO)_2(\mu\text{-}CO_3)(dmpm)_2]$) but under much more forcing conditions (ca. 1700 psi CO_2 at 25°C).[39]

Conclusions

The reaction of ethoxycarbonyl isothiocyanate and carbon disulfide with *trans*-$[RhCl(CO)(dmpm)]_2$ and carbon disulfide with $[Rh_2(CO)_2(\mu\text{-}Cl)(dmpm)_2][BF_4]$ has provided the compounds $[Rh_2Cl_2(CO)\{\mu\text{-}SCNCO_2Et\}(dmpm)_2]$ (**1**), $[Rh_2Cl_2(CO)\{\mu\text{-}SCNC(S)N(CO_2Et)_2\}(dmpm)_2]$ (**2**), $[Rh_2Cl_2(CO)(C_2S_4)(dmpm)_2] \cdot 1/2\ CH_2Cl_2$ (**3**) and $[Rh_2Cl(CO)(C_2S_4)(dmpm)_2][BF_4]$ (**4**), all of which are analogous to those of the related "$Rh_2(dppm)_2$" system.[10c] As in the "$Rh_2(dppm)_2$" studies, the presence of a second metal centre in the "$Rh_2(dmpm)_2$" complex results in the formation of bridging heteroallene species which are coordinated through sulfur to one metal and through carbon to the other. The preliminary X-ray structural determination of the 1:1 adduct, $[Rh_2Cl_2(CO)(\mu\text{-}SCNCO_2Et)(dmpm)_2]$ (1), has confirmed that the ethoxycarbonyl isothiocyanate ligand also interacts with a rhodium atom through the oxygen atom of the acyl fragment, thus forming a five-membered metallocyclic ring. The ability of this oxygen atom to dissociate from the metal centre in solution, providing a site for the coordination of a second heteroallene molecule, has been established from infrared and ^1H NMR spectroscopic data.

The immediate and irreversible reaction of CS_2 with *trans*-$[RhCl(CO)(dmpm)]_2$ and $[Rh_2(CO)_2(\mu\text{-}Cl)(dmpm)_2][BF_4]$ contrasts the behaviour of the analogous dppm compounds which either don't react at all ($[Rh_2(CO)_2(\mu\text{-}Cl)(dppm)_2][BF_4]$) or only in the presence of a vast excess of CS_2 (*trans*-$[RhCl(CO)(dmpm)]_2$). The more favourable binding of CS_2 in the "$Rh_2(dmpm)_2$" system is attributed to the greater basicity of the dmpm ligand which brings about a stronger interaction between the C_2S_4 moiety and the rhodium centes. The basicity of this ligand is also generally reflected in lower $\nu(CO)$ values of the dmpm complexes.

The reaction of *trans*-$[RhCl(CO)(dmpm)]_2$ with CS_2 to yield $[Rh_2Cl_2(CO)(C_2S_4)(dmpm)_2]\cdot 1/2\ CH_2Cl_2$ (3) and the fact that no reaction occurred with CO_2 presumably reflects the difference in electron affinity of the two ligands and the requirement of a highly basic metal centre for reaction to occur with the latter. The disproportionation of C(O)S upon reaction with *trans*-$[RhCl(CO)(dmpm)]_2$ is consistent with the reaction of C(O)S with other complexes involving more than one metal centre.[28,29,34]

The fact that this reaction occurs is a result of the affinity of the soft rhodium centres for sulfur.

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Chapter 4

The Chemical Reduction of Dirhodium-dmpm Complexes and the Subsequent Behaviour of these Species in Solution in the Presence of Carbon Monoxide, Tetrafluoroboric Acid and Chlorinated Reagents

Introduction

Oxidative-addition reactions are of fundamental importance in organometallic chemistry for the catalytic application of transition-metal complexes to organic synthesis.[1,2] As the term implies, the reaction proceeds with an increase in the coordination number and oxidation state of the metal centre(s). Thus, coordinatively unsaturated, electron-rich metal complexes are well suited to this type of process. Our interest in such chemistry has centred around binuclear compounds of rhodium and iridium in efforts to obtain an improved understanding of how the adjacent metals function in the oxidative addition step(s), of the ligand rearrangements that occur, and of the possibility of coupling organic fragments on the adjacent metals. It was surmised that electron-rich, dmpm-bridged, binuclear Rh(0) and Rh(I) compounds, prepared by the reduction of the dmpm-bridged Rh(I) and Rh(II) species from Chapter 2, would be excellent candidates for studying oxidative-addition reactions.

Recent examples of the type of reactivity that is possible from related, zero-valent bimetallic systems involves the complexes $[Ir_2(CO)_3(dppm)_2]$,[3] $[RhIr(CO)_3(dppm)_2]$[4] and $[Ir_2(CO)_3(dmpm)_2]$.[5] The secondary silanes R_2SiH_2 (R= Me, Et, Ph) react with $[Ir_2(CO)_3(dppm)_2]$ to provide the interesting complexes $[Ir_2(H)_2(CO)_2(\mu\text{-}SiR_2)(dppm)_2]$. The mixed-metal complex $[RhIr(CO)_3(dppm)_2]$ reacts with H_2 and H^+ to provide a number of hydride species, the chemistry of which could potentially be applied in the modeling of catalytic processes. The dmpm-bridged diiridium compound has been reported to activate CO_2, providing a carbonate species, $[Ir_2(CO_3)(CO)_2(dmpm)_2]$ which undergoes reversible oxygen transfer with CO.[5]

In this chapter we report on the chemical reduction of the three complexes; *trans*-$[RhCl(CO)(dmpm)]_2$, $[Rh_2Cl_2(CO)_2(\mu\text{-DMAD})(dmpm)_2]$ and $[Rh_2Cl_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$, which were previously described in Chapter 2. The behaviour of the ensuing products in solution in the presence of CO, $HBF_4{\bullet}OEt_2$, acetyl chloride and HCl is also discussed.

Experimental Section

General Comments. General experimental conditions are as described in Chapter 2. Dimethyl acetylenedicarboxylate (DMAD), silver tetrafluoroborate ($AgBF_4$), lithium triethylborohydride ($LiBEt_3H$), acetyl chloride (MeC(O)Cl), thionyl chloride ($SOCl_2$) and tetrafluoroboric acid etherate ($HBF_4{\bullet}OEt_2$) were purchased from The Aldrich Chemical Company. Concentrated hydrochloric acid (HCl) was purchased from BDH Chemicals and sodium borohydride ($NaBH_4$) from Anachemia. Carbon monoxide (C. P. grade) and dihydrogen were purchased from Matheson, ^{13}CO (99%) from Isotec Inc. and hexafluoro-2-butyne (HFB) from SCM Speciality Chemicals. These and all other reagent grade chemicals were used as received. The compounds, *trans*-$[RhCl(CO)(dmpm)]_2$, $[Rh_2Cl_2(CO)_2(\mu\text{-DMAD})(dmpm)_2]$ and $[Rh_2Cl_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ were prepared by the methods described in Chapter 2, and physical measurements were carried out as also described in that Chapter.

Preparation of Compounds. (a) [$Rh_2(CO)_3(dmpm)_2$] (1). An atmosphere of CO was placed over 100 mg (0.165 mmol) of *trans*-[RhCl-(CO)(dmpm)]$_2$ in THF (10 mL) and the resulting orange slurry stirred for 5 min. A one molar solution of NaOH/H_2O (0.33 mL, 0.33 mmol) was then added to the slurry. Complete reaction occurred within 10 to 15 min and was accompanied by dissolution of all solid. After an additional 20 min of stirring, the dark orange solution was placed under vacuum and all solvents were removed. The residue was extracted into benzene or toluene (10 mL) and filtered under dinitrogen through a pad of celite to provide a clear orange solution. Once again, the solvent was removed under vacuum. At this point the product was recovered as an orange-brown solid or redissolved in THF and reacted further. The isolated yield varied between 65% to 75% (60-70 mg). This complex proved to be a nonelectrolyte in THF ($\Lambda(10^{-3}$ M$)= 0.67\ \Omega^{-1}$ cm^2 mol^{-1}). Anal. Calcd for $C_{13}H_{28}O_3P_4Rh_2$: C, 27.8%; H, 5.0%. Found: C, 27.9%; H, 4.8%. Due to the extreme hygroscopic nature of compound **1**, fresh samples were required for suitable elemental analyses.

(b) [$Rh(CO)(\mu$-$CO)(dmpm)]_2$ (2). A solution of compound **1** in THF (5 mL) was prepared in the manner described above using 50 mg (0.083 mmol) of *trans*-[RhCl(CO)(dmpm)]$_2$. Carbon monoxide was bubbled at the rate of ca. 0.5 mL per second through the solution for 1 min, resulting in a slight change in the orange colour. Variable temperature $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR studies in THF-d_8 solution showed the tetracarbonyl complex

[Rh(CO)(μ-CO)(dmpm)]$_2$ (**2**) and a small amount of complex **1** to be the only species present.

(c) [Rh$_2$(CO)$_2$(μ-DMAD)(dmpm)$_2$] (3). The compound, [Rh$_2$Cl$_2$(CO)$_2$-(μ-DMAD)(dmpm)$_2$] (50 mg, 0.067 mmol) and NaBH$_4$ (10 mg, 0.27 mmol) were placed in an oven-dried Schlenk tube under a dinitrogen atmosphere. The addition of 98% EtOH (10 mL) produced a red solution which quickly turned to a deep purple colour. After stirring for 20 min the solvents were removed under vacuum, the product extracted into toluene (10 mL) and the solution filtered under dinitrogen through a pad of celite. Compound **3** was isolated in 60 to 70% yield (27-32 mg) as a deep purple solid upon removal of the solvent under vacuum. Storage of the solid overnight under an atmosphere of N$_2$ led to its decomposition to a dull metallic grey. Subsequent manipulation of the product was carried out in THF, THF-d$_8$ or toluene. Due to its extreme air sensitivity, suitable carbon and hydrogen elemental analysis results were not obtained. This complex proved to be a nonelectrolyte in THF ($\Lambda(10^{-3}$ M$) = 0.25\ \Omega^{-1}$ cm^2 mol^{-1}).

(d) [Rh$_2$(CO)$_2$(μ-HFB)(dmpm)$_2$] (4). To [Rh$_2$Cl$_2$(CO)$_2$(μ-HFB)(dmpm)$_2$] (50 mg, 0.065 mmol) in THF (10 mL) was added two molar equiv of LiBEt$_3$H (0.13 mL of a 1 molar solution in THF). After stirring for 20 min the solvent was removed under vacuum, the residue extracted into toluene (10 mL) and the deep purple solution filtered under dinitrogen through a pad of celite. The product was isolated in ca. 70% yield (32 mg) as a purple powder upon removal of the toluene under vacuum. Prolonged storage of the solid under a dinitrogen atmosphere led to its decomposition. Subsequent manipulation of the product was carried out in THF or toluene solution. Due to the extreme air-sensitivity of the solid, reliable carbon and hydrogen elemental analysis results could not be obtained. The conductivity of this complex was significant ($\Lambda(10^{-3}\ M)= 36\ \Omega^{-1}\ cm^2\ mol^{-1}$) but well below that expected of a 1:1 electrolyte [6] and is presumably due to a small amount of an ionic impurity.

(e) $[Rh_2(BH_4)H(\mu\text{-}CO)(dmpm)_2]$ (5). Method A. The compound $[Rh_2Cl_2(CO)_2(\mu\text{-}DMAD)(dmpm)_2]$ (50 mg, 0.067 mmol) and $NaBH_4$ (30 mg, 0.79 mmol) were placed in a Schlenk tube under an atmosphere of H_2. Tetrahydrofuran (10 mL) was added and the mixture reacted for 16 h. During this time the solution turned from purple to dark brown. The solvent was then removed under vacuum, the brown residue extracted into toluene (10 mL) and the solution filtered through a pad of celite. The solvent was removed from the filtrate under vacuum and compound **5** was isolated as a brown residue in ca. 60% yield. Further manipulation of the product was carried out in THF solution. The conductivity of this complex was significant ($\Lambda(10^{-3}\ M)= 33\ \Omega^{-1}\ cm^2\ mol^{-1}$) but well below that expected of a 1:1 electrolyte [6] and is presumably due to a small amount of ionic impurity. Due to the hygroscopic nature and subsequent decomposition of the solid, reliable elemental analyses were not obtained.

Method B. The above procedure was used to prepare compound **5** from *trans*-$[RhCl(CO)(dmpm)]_2$ (50 mg, 0.082 mmol) and $NaBH_4$ (30 mg, 0.79 mmol). In addition to complex **5**, the $^{31}P\{^1H\}$ NMR and infrared spectra of the reaction mixtures resulting from both methods **A** and **B** revealed the presence of $[Rh_2(CO)_3(dmpm)_2]$ (5-25%).

(f) $[Rh_2(CO)_3(\mu\text{-}H)(dmpm)_2][BF_4]$ (6). A solution of $[Rh_2(CO)_3$-

$(dmpm)_2]$ (**1**) in THF (4 mL) was prepared in the manner described above using 50 mg (0.082 mmol) of *trans*-$[RhCl(CO)(dmpm)]_2$. One equiv of $HBF_4{\bullet}OEt_2$ (8.3 μL, based on a 70% yield of **1**) was added to the solution. The reaction was immediate, producing a colour change from orange to red and some precipitation of product. Compound **6** was not isolated in solid form due to its decomposition. Subsequent characterization of the complex was undertaken spectroscopically in THF or THF-d_8 solution.

(g) $[Rh_2(CO)_4(\mu\text{-}H)(dmpm)_2][BF_4]$ (7). A solution of $[Rh_2(CO)_3(\mu\text{-}H)(dmpm)_2][BF_4]$ (**6**) in THF (4 mL) was prepared in the manner described above using 50 mg (0.082 mmol) of *trans*-$[RhCl(CO)(dmpm)]_2$. Carbon monoxide was slowly passed through the orange solution at a rate of ca. 0.5 mL per second for 1 min, resulting in a change in colour to yellow-orange. Variable temperature $^{31}P\{^1H\}$, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy in THF or THF-d_8 showed compound **7** to be the only species present after reaction. Passing dinitrogen through the solution regenerated the tricarbonyl complex **6** but the complex rapidly decomposed upon attempts to precipitate a solid.

(h) $[Rh_2(CO)_2(\mu\text{-}DMAD)(\mu\text{-}H)(dmpm)_2][BF_4]$ (8). A solution of $[Rh_2(CO)_2(\mu\text{-}DMAD)(dmpm)_2]$ (**3**) in THF (5 mL) was prepared in the manner described above using 50 mg (0.067 mmol) of $[Rh_2Cl_2(CO)_2(\mu\text{-}DMAD)(dmpm)_2]$. One equiv of $HBF_4{\bullet}OEt_2$ (6.2 μL, 0.044 mmol based on a 65% yield of **3**) was added to the solution. Reaction was immediate, producing a colour change from purple to orange with the precipitation of a small amount of orange solid. $^{31}P\{^1H\}$, ^1H NMR and infrared spectroscopy in THF or THF-d_8 revealed compound **8** to be the major product. Attempts to isolate the product in solid form resulted in its decomposition.

(i) $[Rh_2(CO)_2(F_3CC{=}C(H)CF_3)(dmpm)_2][BF_4]$ (9) . The compound $[Rh_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ (4) was prepared as described above (using 50 mg (0.065 mmol) of $[Rh_2Cl_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$) and dissolved in toluene (10 mL). To this was added one equiv of $HBF_4{\bullet}OEt_2$ (6.5 μL, 0.046 mmol based on 70% conversion of the starting material to complex 3). Upon stirring, the reaction mixture quickly changed colour from purple to orange. After 15 min the product settled as an orange-brown oil on the side of the flask. The solvents were removed by cannula under positive N_2 pressure and the oil dried under vacuum for approximately 15 min. Subsequent manipulation and characterization of the complex was carried out in THF or THF-d_8 solution.

(j) $[Rh_2(CO)_3(\mu\text{-CO})(F_3CC{=}C(H)CF_3)(dmpm)_2][BF_4]$ (10). A THF solution (5 mL) of complex **9** was prepared as described above using $[Rh_2Cl_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ (50 mg, 0.067 mmol). A stream of CO was then passed through the solution at the rate of ca. 0.5 mL bubble per second for 3 min, producing a colour change from orange to yellow followed by the precipitation of a yellow solid. Complete precipitation of the compound was effected by the addition of CO-saturated diethyl ether (25 mL) and cooling of the mixture to 0°C. The solvents were removed by cannula under positive N_2 pressure and the product was dried under a slow stream of CO. Recrystallization of this solid from CO-saturated THF/diethyl ether yielded 37 mg (67%) of compound **10** as a yellow powder. This complex proved to be a 1:1 electrolyte in acetonitrile

($\Lambda(10^{-3}$ M)= 164 Ω^{-1} cm^2 mol^{-1}). Anal. Calcd for $BC_{18}F_{10}H_{29}O_4P_4Rh_2$: C, 25.7%; H, 3.5%. Found: C, 25.5%; H, 3.5%.

Reaction of complexes with HCl, $SOCl_2$ and acetyl chloride. The appropriate reagent, (up to 10 molar equiv), was added via syringe to a solution (THF or toluene) of the complex, either $[Rh_2(CO)_3(dmpm)_2]$ (**1**), $[Rh_2(CO)_2(\mu\text{-DMAD})(dmpm)_2]$ (**3**) or $[Rh_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ (**4**), prepared as described above and allowed to stir under an atmosphere of dinitrogen for several hours. Subsequent characterization of the products was carried out by $^{31}P\{^1H\}$ NMR on the reaction mixture or by $^{31}P\{^1H\}$ NMR and infrared spectroscopic methods on THF or CH_2Cl_2 solutions (or their deuterated counterparts) of the residue.

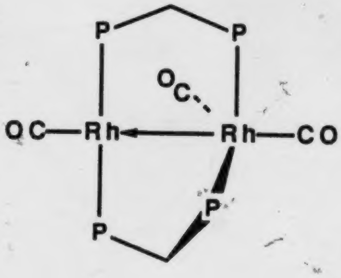
The reaction of $[Rh_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ (**4**) with acetyl chloride entailed the addition of two equiv of the reagent (7.5 μL) to a purple toluene solution (8 mL) of **4** (0.052 mmol based on 80% conversion of $[Rh_2Cl_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$; 50 mg, 0.065 mmol). The solution colour changed to orange-yellow within 15 min. Stirring was continued for an additional 15 min, the solvent was then removed under vacuum, the residue washed with hexane (20 mL) and the products dried under dinitrogen. The spectroscopic characterization of the products was carried out in THF or THF-d_8.

Results and Discussion

(a) Reduction Reactions. The reduction of *trans*-$[RhCl(CO)(dmpm)]_2$ is carried out under an atmosphere of CO using a one molar solution of NaOH/H_2O. The product, $[Rh_2(CO)_3(dmpm)_2]$ (**1**), is isolated in reasonable yield (65%) as an air and moisture-sensitive orange-brown residue. This species is highly reactive and must be kept out of contact with chlorinated solvents to prevent reformation of the starting material, *trans*-[RhCl(CO)-(dmpm)]$_2$. It oxidatively adds reagents such as acetyl chloride to yield *trans*-[RhCl(CO)(dmpm)]$_2$ or HCl and $SOCl_2$ to yield [$RhCl_2$(CO)(dmpm)]$_2$. Complex **1** was also prepared from the reaction of sodium napthalenide or sodium borohydride with *trans*-[RhCl(CO)(dmpm)]$_2$ under a CO atmosphere. However, due to impurities which are also formed in the latter two methods, the preparation from NaOH/H_2O represents the most reliable procedure.

The reaction with NaOH/H_2O presumably involves the formation of an intermediate species containing an "-OHCl" moiety in which the hydroxide group is hydrogen-bonded to the chloride, much that found in the dppm analogues [$Rh_2(CO)_2$(μ-OH•Cl)(dppm)$_2$] [7] or [$Ir_2(CO)_2$(μ-OH•Cl)-(dppm)$_2$].[8] The iridium species is prepared under similar conditions from the reaction of *trans*-[IrCl(CO)(dppm)]$_2$ with NaOH. Formation of the final "Rh_2(dmpm)$_2$" product under an atmosphere of CO can be rationalized by the transfer of the bridging hydroxide ligand to a coordinated carbonyl ligand and subsequent loss of HCl and CO_2. Alternatively, as suggested by Otsuka et al.[9] for mononuclear rhodium-hydroxide species, the reaction may proceed via hydroxide dissociation and nucleophilic attack at a carbonyl group. Deprotonation of the resulting M-CO_2H moiety by excess base, loss of CO_2, and addition of two mole equiv of CO would then provide the final tricarbonyl species. A less likely prospect involves the formation of a dihydroxide species which undergoes nucleophilic attack of both hydroxide ligands at two carbonyl ligands. Loss of two mole equiv of CO_2 and one mole equiv of H_2 from this intermediate, under an atmosphere of CO, should then provide the final product. Although a complex containing the μ-OH•Cl moiety seems to be a likely prospect in this reaction, it should be stressed that none of the suggested intermediates has been observed during the formation of compound **1**.

Infrared and variable-temperature NMR data (see Tables 4.1 and 4.2) have shown complex **1** to be as illustrated. This formulation is in turn



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based on that found for the congeners $[Rh_2(CO)_3(dppm)_2]$,[10] $[Rh_2(CO)_3\{(PhO)_2PN(Et)P(OPh)_2\}_2]$,[11] $[CoRh(CO)_3(dppm)_2]$ [12,13] and $[RhIr(CO)_3(dppm)_2]$ [4] and suggested for $[Ir_2(CO)_3(dppm)_2]$ [8] and $[Ir_2(CO)_3(dmpm)_2]$.[5] The more salient features of this structural type include:

1. Different coordination spheres about the metal centres consisting of mixed-valence M(+1)/M(-1) centres in which the M(-1) atom has been likened to a pseudohalide that bonds to the M(+1) centre through a dative metal-metal bond.[4,12] The coordination spheres about the metal centres are best considered as distorted square planar for M(+1) and distorted

Table 4.1. Infrared Spectroscopic Data for the Compounds in Chapter 4.[a]

		Nujol, cm^{-1}		THF solution, cm^{-1}	
no.	compound	ν(CO)	others	ν(CO)	others
1	$[Rh_2(CO)_3(dmpm)_2]$	1953(vs), 1912(s), 1824 (m)		1960(m), 1925(s), 1847(m)	
2	$[Rh(CO)(\mu\text{-}CO)(dmpm)]_2$			1962(m), 1926(m), 1914(m, sh), 1847(m)	
3	$[Rh_2(CO)_2(\mu\text{-}DMAD)(dmpm)_2]$			1956(s), 1935(m), 1685(m)^b	
4	$[Rh_2(CO)_2(\mu\text{-}HFB)(dmpm)_2]$			1963(s), 1942(m)	
5	$[Rh_2BH_4(H)(\mu\text{-}CO)(dmpm)_2]$	1744(s)	2387(m),^{c} 2364(m),^{c} 1147(m)^c	1747(s) 1707(vs)^d	2391(m),^{c} 2370(m),^{c} 1149(m)^c
6	$[Rh_2(CO)_3(\mu\text{-}H)(dmpm)_2][BF_4]$			1980(m, sh), 1960(vs), 1895(w)	
7	$[Rh_2(CO)_4(\mu\text{-}H)(dmpm)_2][BF_4]$			1985(s), 1958(s)	
8	$[Rh_2(CO)_2(\mu\text{-}H)(\mu\text{-}DMAD)(dmpm)_2][BF_4]$			1988(s), 1974(m), 1743 (m)^b	
9	$[Rh_2(CO)_2(F_3CC{=}C(H)CF_3)(dmpm)_2][BF_4]$			1995(m), 1973 (m), 1964(m), 1943(w)	1608(w)^e
10	$[Rh_2(CO)_3(\mu\text{-}CO)(F_3CC{=}C(H)CF_3)(dmpm)_2][BF_4]$	2044 (vs), 2014(vs), 1988(vs), 1765(vs)	1600 (m)^e	2043(m), 2020(s), 1993(m, br), 1792(w, br)	

[a] Abbreviations used: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder. [b] ν(CO) of CO_2Me. [c] $\nu(MBH_4)$. [d] $\nu(^{13}CO)$. [e] ν(CC).

Table 4.2. NMR Spectroscopic Data for the Compounds in Chapter 4.[a,b]

	$\delta(^{31}P(^{1}H))^{c}$	$\delta(^{13}C(^{1}H))^{d}$	$\delta(^{19}F)$	$\delta(^{1}H)$		
compound				P-CH_3	-CH_2-	others
1	-13.55(137 Hz)	198.7(s, br)		1.54(s, 24H)	2.75(m, 4H)	
	-5.71(dt, 117.3, 78.8 Hz),^{e}	184.4(d, br, $^{1}J_{C\text{-}Rh}$= 72 Hz),^{f}		1.61(s, 12H),^{e}	2.79(m, 4H)^{e}	
	-19.62(dt, 155.7, 78.8 Hz)^{e}	205.4(d, br, $^{1}J_{C\text{-}Rh}$= 69 Hz),^{f}		1.47(s, 12H)^{e}		
		207.7(m, $^{1}J_{C\text{-}Rh}$= 76 Hz)^{f}				
2	-15.5(m)	198.4(dd, $^{1}J_{C\text{-}Rh}$= 90.6 Hz,		1.52(s, 24H)^{e}	3.06(m, 4H)^{e}	
	14.38(99.8 Hz)^{e}	$^{2}J_{C\text{-}Rh}$ = 3 Hz),^{f}				
		245.3(tt, $^{1}J_{C\text{-}Rh}$= 28 Hz,				
		$^{2}J_{C\text{-}P}$ ~ 28 Hz)^{f}				
3	-7.17(144 Hz)			1.56(s, 12H),	2.68(m, 4H)	3.41(s, 6H)^{g}
				1.53(s, 12H)		
4	-9.30(142 Hz)	197.54(dm, $^{1}J_{C\text{-}Rh}$ = 58.4 Hz)	-48.8(s)	1.61(s, 12H),	2.45(m, 4H)	
				1.50(s, 12H)		
5^{h}	3.53(107 Hz)	238.23(tq, $^{1}J_{C\text{-}Rh}$= 42.6 Hz,		1.55(s, 12H),	1.77(m, 4H)	-1.1, -1.7(m, br)^{i}
		$^{2}J_{C\text{-}P}$= 8.3 Hz)		1.49(s, 12H)		
				1.55(s, 12H),^{e}	2.17(m, 2H),^{e}	-3.55, -5.20(m, br)^{e,i}
				1.49(s, 12H)^{e}	2.00(m, 2H)^{e}	
6	6.49(98 Hz)	194.1(s)		1.76(s, 24H)	2.87(m, 4H)	-9.33(m, 1H,
		188.3(m),^{f}				$^{1}J_{H\text{-}Rh}$= 25.2 Hz,
		196.4(tq, $^{1}J_{C\text{-}Rh}$= 34.1 Hz, $^{2}J_{C\text{-}P}$ = 7.4 Hz)^{f}				$^{2}J_{H\text{-}P}$= 11.5 Hz)^{j}

Table 4.2 (continued)

no	δ(^{31}P(^{1}H))	δ(^{13}C(^{1}H))	δ(^{19}F)	δ(^{1}H)		
				P-CH$_3$	-CH$_2$-	others
7	1.19(83.2 Hz)	199.4(dm, J= 67 Hz)^f		1.78(s, 24H)^k	3.32(m, 4H)^k	-7.65(m, 1H,
	1.93(81.5 Hz)^k					$^1J_{H\text{-}Rh}$ = 21.9 Hz,
						$^2J_{H\text{-}P}$ = 11.5 Hz)^{j,k}
8	-4.2(104 Hz)			1.68(s, 12H),	3.1(m, 4H)	-11.53(m, 1H,
				1.63(s, 12H)		$^1J_{H\text{-}Rh}$= 22.5 Hz)^j
9	-0.5(m)	196.14(d, $^1J_{C\text{-}R}$ = 50 Hz),^{f}	-51.8(m, 3F),^{k}	1.77(m, 12H),	2.92(m, 2H),	5.85(m, br, 1H)^l
	-1.0(m)^k	179.03(d, $^1J_{C\text{-}Rh}$= 74 Hz)^f	-59.9(m, 3F),^{k}	1.67(m, 12H)	2.74(m, 2H)	
			-149.5(s br, 4F)^k			
10	4.66(m, unresolved),	234.6(m, five line	-51.48(qr, 3F,	1.88(t, 6H),^{k}	3.2(m, 2H),^{k}	6.10(qr, 1H,
	2.60(dt, 87.7, 43 Hz)	multiplet upon (^{31}P),^{f}	$^5J_{F\text{-}F}$ = 12.2 Hz),^{k}	1.82(t, 6H,	2.9(m, 2H)^k	$^3J_{H\text{-}F}$ = 10 Hz)^{k,l}
			199.0(m),^{f}	-59.36(dqr, 3F,	$^2J_{H\text{-}P}$ = 3.0 Hz),^{k}	
	6.12(dt, 76, 40 Hz),^{k}	198.1(m),^{f}	$^5J_{F\text{-}F}$= 12.2 Hz,	1.67(t, 6H),^{k}		
	3.50(dt, 84, 40 Hz)^k	190.8(ddt, $^1J_{C\text{-}Rh}$= 69.1 Hz,	$^3J_{F\text{-}H}$= 10 Hz),^{k}	1.38(t, 6H,		
		$J_{C\text{-}P}$ = 14 Hz, J= 12 Hz)^f	149.5(s, br, 4F)^k	$^2J_{H\text{-}P}$ = 3.8 Hz)^k		

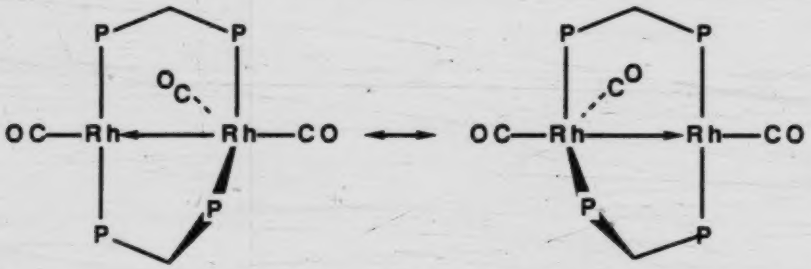
[a] Ambient temperature in THF-d_8 unless otherwise noted. [b] Abbreviations used: s, singlet; d, doublet; t, triplet; qr, quartet; q, quintet; m, multiplet; dd, doublet of doublets; dt, doublet of triplets; dqr, doublet of quartets; dm, doublet of multiplets; ddt, doublet of doublet of triplets; tt, triplet of triplets; tq, triplet of quintets; br, broad. [c] Vs 85% H_3PO_4, numbers in parentheses represent the separation in hertz between the major peaks in the second-order spectrum of the complex. [d] ^{13}CO enriched samples. [e] -75°C. [f] -85°C. [g] CO_2Me. [h] ^{11}B NMR of 5 referenced to $BF_3{\bullet}OEt_2$ in THF-d_8 : δ -18.0(q, $^1J_{B\text{-}H}$ = 87 Hz) and ^{11}B(^{1}H) NMR, δ -17.7(s , br at -40°C). [i] MBH_4. [j] M-H. [k] -40°C. [l] C(H)CF_3.

trigonal bipyramidal for M(-1). This bonding description is based on the results of structural characterizations of the mixed-metal complexes, $[RhIr(CO)_3(dppm)_2]$ [4] and $[CoRh(CO)_3(dppm)_2]$.[13] Alternatively, as suggested for the homobimetallic species $[Rh_2(CO)_3(dppm)_2]$ [10] and $[Ir_2(CO)_3(dmpm)_2]$,[5] the metal atoms can be considered as formally M(0) centers with a normal metal-metal bond.

2. Phosphorus atoms which are mutually cis on one metal and mutually trans on the other.
3. Three carbonyl ligands, two of which are terminally coordinated, one to each of the metal centres and the third which interacts strongly with one metal centre and much more weakly with the second metal, in a semi-bridging manner.

Each of these points can be addressed for the case at hand upon close examination of the spectroscopic data. Both solution and solid-state infrared spectra of complex **1** reveal three strong bands in the carbonyl region. The first two, at 1953 cm^{-1} and 1912 cm^{-1}, are consistent with terminally coordinated carbonyl ligands while the third band at 1824 cm^{-1} is somewhat lower in frequency suggesting a possible interaction of the carbonyl ligand with both metal centres in a bridging capacity. The same band pattern and similar values have been reported for both homo- and heterobimetallic $[MM'(CO)_3(dppm)_2]$ complexes, (M= Co, Rh, Ir, M'= Rh; M= M'= Ir)[4,8,10,13] suggesting that compound **1** has a closely related structure.

At room temperature the $^{31}P\{^1H\}$ NMR spectrum of **1**, shown at the top of Figure 4.1, contains a single broad resonance with two principal peaks. The resonance is reminiscent of an AA'A''A'''XX' pattern associated with a symmetrical "Rh_2(diphosphine)$_2$" complex but the broadness of the signal suggests that there is some fluxionality within the molecule. This was confirmed in the low temperature $^{31}P\{^1H\}$ NMR spectrum (-75°C, bottom of Figure 4.1) where the signal appeared as an AA'BB'XY pattern. Thus, we attribute the appearance of the room temperature spectrum to an equilibration of all phosphorus atoms, occurring by rapid movement in and out of mutually cis and trans positions. Evidence for similar cis-trans movement of the diphosphines was found in the related $[Ir_2(CO)_3(dmpm)_2]$.[5] As shown below for two of the static structures, the environment on each metal is proposed to alternate between a four-coordinate, square-planar rhodium and five-coordinate, distorted trigonal-bipyramidal rhodium centre. This also



requires the exchange of CO ligands from one centre to the other. Consistent with this hypothesis, the $^{13}C\{^1H\}$ NMR spectrum at room temperature contains a single broad resonance at δ 198.7 in the carbonyl region (complete CO exchange was not observed in the mixed metal systems [4,13]).

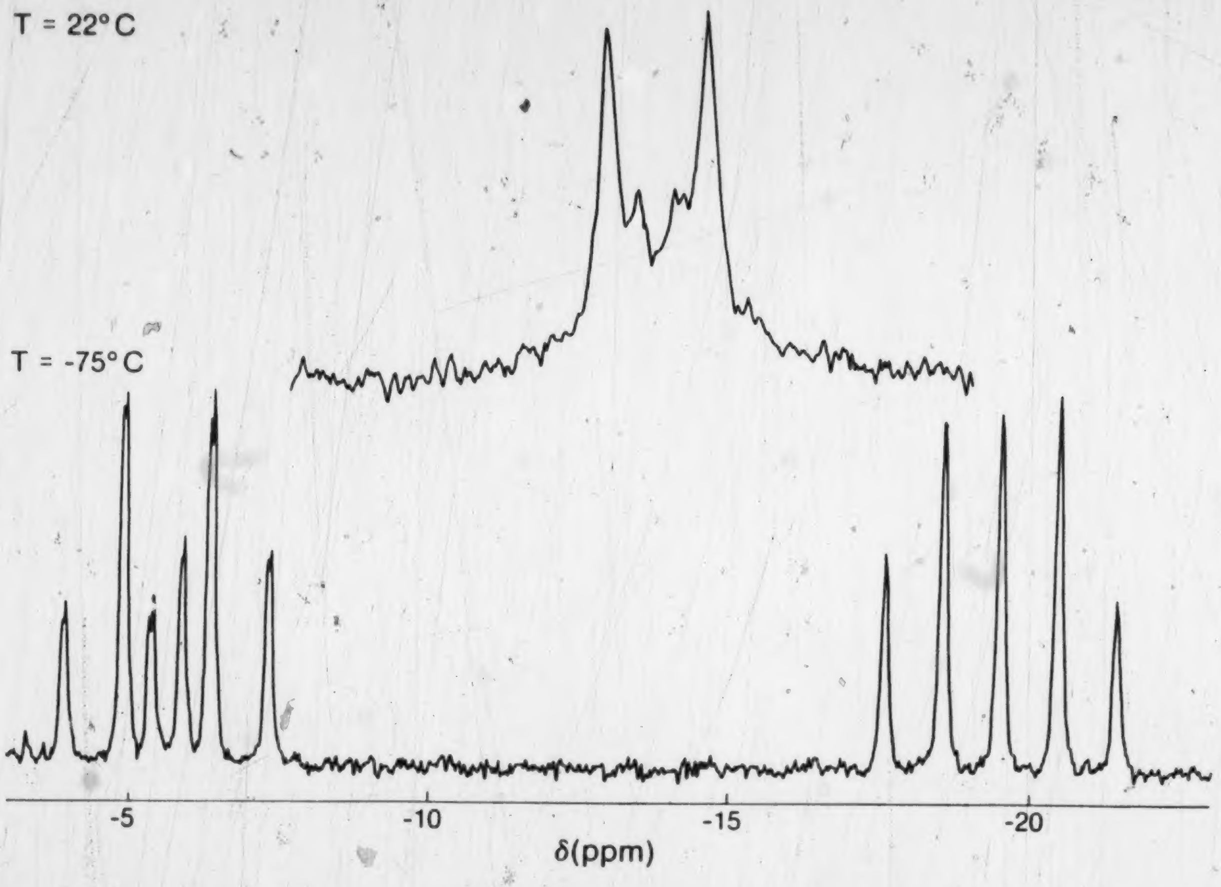
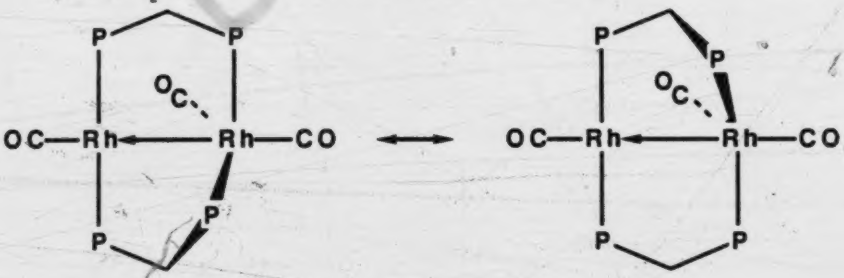


Figure 4.1. The $^{31}P\{^1H\}$ NMR spectrum of $[Rh_2(CO)_3(dmpm)_2]$ (1) at 22° and -75°C

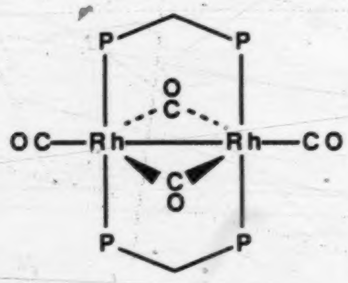
At low temperature (-75°C), the appearance of an AA'BB'XY pattern ($^{31}P\{^1H\}$ NMR spectrum, two sets of doublets of pseudotriplets, Figure 4.1) indicates that the two rhodium environments are now distinct and the phosphorus atoms on the same metal are chemically equivalent. This suggests a structure in which the two phosphorus atoms on the five-coordinate metal centres are in identical cis positions while the two on the four-coordinate metal centre remain trans to each other. Alternatively, one side of the molecule may still be somewhat fluxional and the same two phorphorus atoms are equilibrated by virtue of their rapid movement in and out of a cis position as shown below.



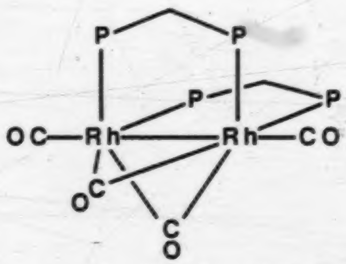
The $^{13}C\{^1H\}$ NMR spectrum of **1** at -85°C contains three resonances in the CO region (δ 184.4, $^1J_{C\text{-}Rh}$= 72 Hz; δ 205.4, $^1J_{C\text{-}Rh}$= 69 Hz; δ 207.7, $^1J_{C\text{-}Rh}$ca. 76 Hz) with relative intensities of 1:1:1. The one-bond rhodium-carbon coupling is evident in all three resonances but any other interactions are obscured by a lack of resolution. Phosphorus-decoupling the spectrum does little to improve the resolution, suggesting that the CO ligands are still somewhat fluxional at this temperature. The obvious fluxionality of compound **1** in solution reflects the general behaviour of the [MM'$(CO)_3$(diphosphine)$_2$] class of compounds as well as many of the other "$Rh_2(dmpm)_2$" complexes prepared in the course of our investigations (see Chapter 2). The complete alternation of configuration between the metal centres of the dmpm species is no doubt aided by the small size of the diphosphine ligands.

In solution, under excess CO, compound **1** was found to be in equilibrium with a small amount of the labile tetracarbonyl species $[Rh(CO)(\mu\text{-}CO)(dmpm)]_2$ (**2**). Replacement of the CO atmosphere with dinitrogen regenerates the starting material **1**. The ease with which the fourth carbonyl ligand is removed from **2** is reminiscent of the behaviour observed for $[Ir(CO)_2(dppm)]_2$ which also loses CO when placed under an atmosphere of N_2.[8] In contrast to compound **2**, however, removal of CO from the "$Ir_2(dmpm)_2$" analogue, $[Ir(CO)_2(dmpm)]_2$,[5] is more difficult and requires heating in the presence of Me_3NO. All other things being equal, the basic iridium metal-centres in this latter complex should interact more strongly than the rhodium centres of **2** with π–acid ligands such that the complex does not lose CO as readily.[14]

Due to the equilibrium between compounds **1** and **2** under excess CO, the room temperature spectra of the latter are somewhat deceiving and the presence of the new species **2** is hard to discern. Only slight changes occur in the solution-infrared spectrum with the appearance of a new shoulder at 1914 cm^{-1}, in addition to the original three bands of **1** (see Table 4.1). In the $^{31}P\{^1H\}$ NMR spectrum, a broad, unresolved resonance, much like that of $[Rh_2(CO)_3(dmpm)_2]$ (**1**), appears at δ -15.5 . At -75°C, however, one major resonance appears in the $^{31}P\{^1H\}$ NMR spectrum at δ 14.4 (assigned to compound **2**) which has the typical AA'A"A'"XX' pattern of a symmetrical "$Rh_2(diphosphine)_2$" complex. A much smaller amount of compound **1** is also present, indicating that the equilibrium between **1** and **2** has been shifted towards a higher concentration of **2** under these conditions. The change is also evident in the carbonyl region of the $^{13}C\{^1H\}$ NMR spectrum (-85°C) where resonances due to **1** are very low in intensity. New resonances appearing at δ 245.3 and δ 198.4 in a 1:1 ratio have been assigned to compound **2** (Figure 4.2). Their chemical shifts indicate the presence of both bridging and terminal CO ligands, respectively. These data are consistent with either trans-trans diphosphine geometry (**A**) or cis-cis diphosphine geometry (**B**). We favour geometry **B**



A



B

based on careful interpretation of the low temperature $^{13}C\{^1H\}$ and $^{13}C\{^{31}P\}\{^1H\}$ NMR data and note that the cis-cis diphosphine form has been reported for the cobalt analogues of **2**, $[Co(CO)(\mu\text{-}CO)(dppm)]_2$ [15] and $[Co(CO)(\mu\text{-}CO)(dmpm)]_2$[15b] and the isoelectronic iridium complexes $[Ir(CNR)(\mu\text{-}CNR)(dmpm)]_2$ and $[Ir(CNR)(\mu\text{-}CN(BH_3)R)(dmpm)]_2$ (R= 2, 6-$Me_2C_6H_3$).[16] In Figure 4.2, the lowerfield signal at δ 245.3 is assigned to the bridged carbonyl ligands and appears as a multiplet containing five lines in the proton decoupled spectrum. This pattern is rationalized in

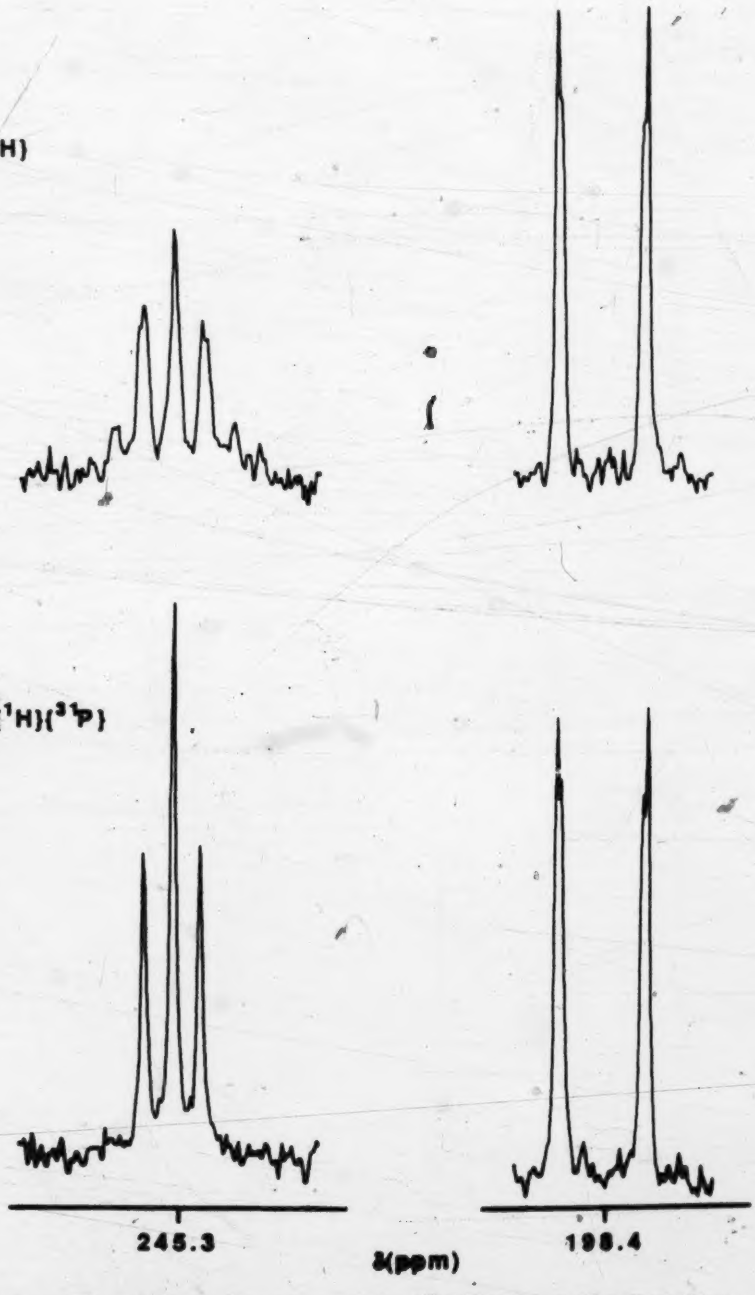


Figure 4.2. The carbonyl region of the $^{13}C\{^1H\}$ and $^{13}C\{^1H\}\{^{31}P\}$ NMR spectra of $[Rh(CO)(\mu\text{-}CO)(dmpm)]_2$ (2) at -85°C.

terms of an overlapped triplet (coupling of the carbon atom with two chemically equivalent rhodium atoms) of triplets (coupling with the two chemically equivalent phosphorus atoms which are more or less trans to the bridging CO ligand). This hypothesis requires that ${}^{2}J_{C\text{-}P}$ (trans) and ${}^{1}J_{C\text{-}Rh}$ be similar in magnitude (ca. 28 Hz). It also requires that the coupling between the bridging carbonyl carbon atom and the two phosphorus atoms which are more or less cis to it be relatively weak. Consistent with this proposal, ${}^{2}J_{C\text{-}P}$ (cis) in similar binuclear diphosphine complexes[4,17,18] is typically found to be less than 17 Hz and is often too weak to be resolved. In structure **A** then, only one coupling interaction on the order of 28 Hz, that of ${}^{1}J_{C\text{-}Rh}$, would be expected and we interpret the stronger C-P interaction to mean that the bridging CO ligands are situated more or less trans to two of the diphosphine ligands as in structure **B**. As shown in Figure 4.2, phosphorus-decoupling the spectrum reduces the multiplet to a well resolved triplet (${}^{1}J_{C\text{-}Rh}$= 28 Hz), thus confirming that the second 28 Hz coupling is indeed due to a C-P interaction and indicating that coupling between the carbon atoms of the terminal and bridging CO ligands must be too small to be observed.

The carbon atoms of the terminal carbonyl ligands are strongly coupled to a single rhodium atom and appear as a doublet at δ 198.4 (${}^{1}J_{C\text{-}Rh}$= 90.6 Hz). Two-bond C-P coupling is apparently too weak to be resolved and C-C coupling is not observed at all. In the phosphorus-decoupled spectrum the signal, now a doublet of doublets, is much sharper and we are able to observe the weaker two-bond coupling of carbon to the second rhodium as well (${}^{2}J_{C\text{-}Rh}$= 3 Hz). This two-bond interaction is usually too small to be observed except in cases where the carbonyl ligand is collinear with the metal-metal bond.[19-22]

Due to the equilibrium between compounds **1** and **2** and to the predominance of **1** in solution at room temperature, we have been unable to determine whether the bridged CO ligands of compound **2** remain so at higher temperature or whether, as seen for the cobalt analogues, they become terminally coordinated.[15b] It is noted that the "all terminal" tetracarbonyl-diiridium analogue of **2**, $[Ir(CO)_2(\underline{d}mpm)]_2$, has been isolated at room temperature but it does not appear from the preliminary report that the two dmpm ligands are coordinated in a cis-cis geometry.[5]

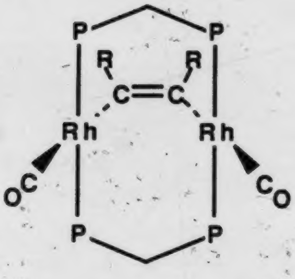
The $NaBH_4$/EtOH reduction of $[Rh_2Cl_2(CO)_2(\mu\text{-DMAD})(dmpm)_2]$ and the $LiBEt_3H$/THF reduction of $[Rh_2Cl_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ result in the removal of the chloride ligands and formation of symmetrical alkyne-bridged complexes with the formula $[Rh_2(CO)_2(\mu\text{-alkyne})(dmpm)_2]$ (**3**, alkyne= DMAD; **4**, alkyne= HFB). The same results may be obtained from the addition of one equiv of DMAD or HFB to $[Rh_2(CO)_3(dmpm)_2]$ (**1**), however, this method requires strict control of the stoichiometry in order to avoid reaction of the products with a second equiv of alkyne. (These subsequent reactions with two equiv of DMAD or HFB are discussed in Chapter 5.)

The two new alkyne species **3** and **4** are stable under dinitrogen for extended periods of time but are readily re-oxidized to their respective starting materials in the presence of chlorinated solvents or hydrochloric acid. Both compounds add CO to provide a number of uncharacterized products. The attempted recrystallization of either compound from

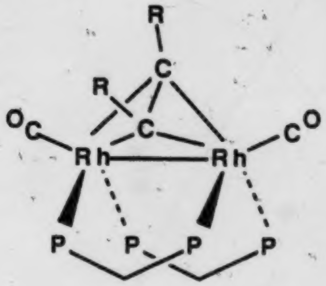
THF/pentane or THF/hexane resulted in their decomposition, but they are isolable as deep purple powders upon removal of the solvents under vacuum. Up to a point, the re-introduction of solvent regenerates the purple solution but extended exposure of the solid to vacuum results in a colour change from purple to a dark metallic grey and eventually leads to its decomposition. From these results it would appear that **3** and **4** are solvated and rapidly decompose once the solvent molecule is removed. This behaviour, in addition to their extreme air-sensitivity, has limited the characterization of these compounds to solution spectroscopy.

Infrared data reveal the presence of two terminal carbonyl bands for each of **3** and **4** in the range 1963 to 1935 cm^{-1} (Table 4.1). The infrared spectrum of complex **3** exhibits an additional band at 1685 cm^{-1} due to the carboxylate group of DMAD. The symmetrical nature of **3** and **4** is evident from the appearance of a second order resonance with an AA'A"A'"XX' pattern in the $^{31}P\{^1H\}$ NMR spectrum (δ -7.17 for **3**, δ -9.30 for **4**). Complex **4** exhibits a singlet in the ^{19}F NMR spectrum (δ -48.8) due to the six chemically equivalent fluorine atoms of the HFB ligand.

Unfortunately, the actual configuration of the alkyne ligands in **3** and **4** could not be determined from the available spectroscopic data. The two possible geometric forms are as illustrated on the following page. Structure **C** contains a formally dianionic, four-electron donor alkyne ligand coordinated parallel to the metal-metal vector, implying two Rh(+I) centres. In structure **D**, in which the metal centres are considered to be Rh(0), a neutral, four-electron donor alkyne ligand is coordinated perpendicular to the metal-metal vector. Generally, in



C



D

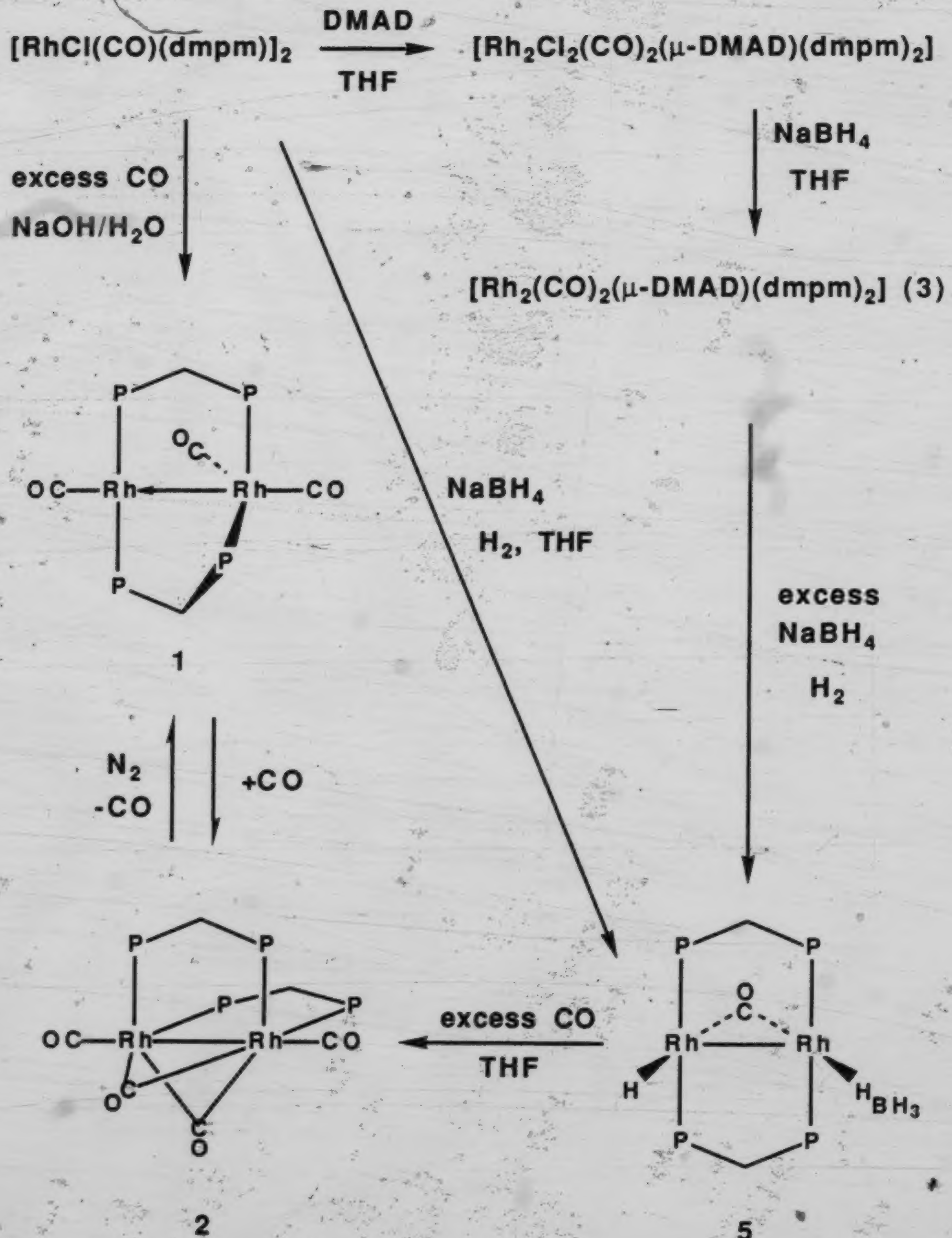
"Rh_2(diphosphine)$_2$" complexes, electrophilic alkynes such as DMAD and HFB are coordinated in the parallel mode C.[18b,23,24] If this were so in the present examples then no change in the alkyne coordination mode would have occurred upon reduction of the starting materials, [$Rh_2Cl_2(CO)_2$-(μ-DMAD)(dmpm)$_2$] and [$Rh_2Cl_2(CO)_2$(μ-HFB)(dmpm)$_2$]. The products, **3** and **4**, would then be isoelectronic with the palladium and platinum complexes, [MM'Cl_2(μ-alkyne)(dppm)$_2$] (M= M'= Pt, alkyne= HFB; M= M'= Pd, alkyne= HFB, DMAD; M= Pt, M'= Pd, alkyne= DMAD)[25-27] which are known to have structure C. However, in the closely related example [$Rh_2(CO)_2$(μ-PhC_2Ph)(dppm)$_2$],[28] the dppm ligands have been shown by X-ray crystallography to be cis to each other and the infrared, ^1H, and $^{31}P\{^1H\}$ NMR data of this species are very similar to that of **3** and **4**. Confirmation of either trans, trans- or cis, cis-"M_2(dmpm)$_2$" geometry in diiridium complexes has been made possible by examination of the ν(P-C) stretching region (910-970 cm^{-1}) of the infrared spectrum, the former configuration giving rise to a single sharp band at 940 cm^{-1} and the latter giving rise to two bands or a very broad band at lower energy.[16b] We have not found a similar correlation to be evident in the spectra of complexes **3** or **4** and given the demonstrated ability of alkyne ligands to change coordination modes,[29-34] we cannot say with confidence which is the correct form in compounds **3** and **4**.

In an effort to detect the possibility that a change in alkyne ligand coordination might result in a chemical shift change in the $^{31}P\{^1H\}$ NMR spectrum, the preparation of both **3** and **4** were monitored at low temperature (-78°C). A chemical shift change upon alkyne re-orientation has been observed during the reaction of DMAD with $[Ir_2(CO)_3(dppm)_2]$ [33] and $C_6H_5C_2H$ with $[Rh(CO)(\mu\text{-}H)(dppm)]_2$.[32b] Although similar changes in the above "$Rh_2(dmpm)_2$" complexes were not detected, the re-orientation cannot be ruled out since the small steric constraints of dmpm ligands could very well provide for alkyne rearrangement which is too rapid to be observed. Alternatively, $^{13}C\{^1H\}$ NMR chemical shift values of the alkyne carbon atoms may be useful for determining the mode of coordination since there appears to be a significant difference in the range (δ 120-150 for type **C** and δ 60-100 for type **D**)[32b,35-38] within which each type occurs. However, using natural abundance ^{13}C, we could not clearly identify the appropriate resonances for either **3** or **4** in the $^{13}C\{^1H\}$ NMR spectrum.

Surprisingly, complex **3** undergoes a subsequent reaction upon long term exposure to $NaBH_4$ (16 h under N_2 atmosphere), producing a new resonance in the $^{31}P\{^1H\}$ NMR spectrum at δ 3.53 (AA'A"A"'XX' pattern). The preparation of this second species is optimized by reacting $[Rh_2Cl_2(CO)_2(DMAD)(dmpm)_2]$ directly with an excess of $NaBH_4$ in THF solution under an atmosphere of H_2. Removal of the solvents under vacuum and workup of the product in toluene provides an air-sensitive, sticky-brown residue which, based on solution infrared and NMR data, is formulated as [$Rh_2(BH_4)H(\mu\text{-}CO)(dmpm)_2$] (**5**). While trying to determine whether DMAD was still incorporated in the reaction product it was found that *trans*-[RhCl(CO)(dmpm)]$_2$ reacts under similar conditions with the same outcome. These reactions are summarized in Scheme 4.1. The structure of **5** which is illustrated in Scheme 4.1 is not intended to imply the mode of BH_4^- coordination to the metal atom. In other BH_4^- containing species the BH_4^- unit has been observed to covalently bind through one, two or three hydrogen atoms to one or two metal centre(s).[39-49] Rapid intramolecular proton site exchange can occur in a number of ways in these complexes [43,44,45a,50] and, as is often the case,[40-44,49,50,51,52] the BH_4^- moiety in complex **5** appears to be highly fluxional. Unfortunately, low temperature NMR spectroscopic investigations on complex **5** did not provide a clearer picture of the manner in which the BH_4^- moiety is bound and this question remains unanswered.

Although a considerable effort has been expended in the characterization of compound **5**, the means by which it is produced and the nature of the nonmetal products remains unknown. As illustrated in the scheme, the complex is proposed to have an "A-frame" structure with the carbonyl ligand at the apex of the letter "A". This bridging CO ligand gives rise to a single resonance in the CO region of the $^{13}C\{^1H\}$ NMR spectrum at δ 238.23 (triplet of quintets, $^1J_{C\text{-}Rh}$= 42.6 Hz, $^2J_{C\text{-}P}$= 8.3 Hz) and a band at 1747 cm^{-1} ($\upsilon(^{13}CO)$= 1707 cm^{-1}) in the solution infrared spectrum.

Scheme 4.1


$[RhCl(CO)(dmpm)]_2$
DMAD
THF
$[Rh_2Cl_2(CO)_2(\mu\text{-}DMAD)(dmpm)_2]$
$NaBH_4$
THF
$[Rh_2(CO)_2(\mu\text{-}DMAD)(dmpm)_2]$ (3)
excess CO
$NaOH/H_2O$
$NaBH_4$
H_2, THF
excess
$NaBH_4$
H_2
1
N_2
-CO
+CO
excess CO
THF
2
5
P
Rh
OC
CO
H
H_{BH_3}

The A-frame assignment is based on the isolobality of X^- with BH_4^- [39] and the similarity between the ν(CO) value of complex **5** and those of the bridging-monocarbonyl A-frame complexes $[Rh_2(X)_2(\mu\text{-}CO)(dppm)_2]$ (X= Cl, υ(CO)= 1745 cm^{-1}; X= Br, υ(CO)= 1745 cm^{-1}; X= I, υ(CO)= 1755 cm^{-1}, (Nujol)).[53]

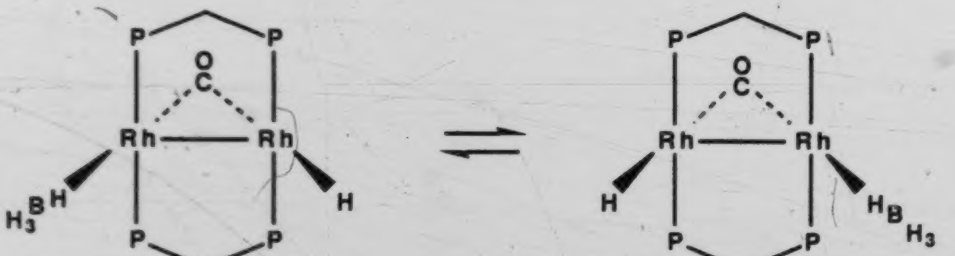
The formation of a monocarbonyl species implies the loss of one equiv of CO from either *trans*-$[RhCl(CO)(dmpm)]_2$ or $[Rh_2(CO)_2(\mu\text{-}DMAD)(dmpm)_2]$ (**3**) during the reaction. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture indicates the presence of $[Rh_2(CO)_3(dmpm)_2]$ (**1**) in amounts (ca. 5-25 %) which are consistent with the reaction of two equiv of free CO with **5** to produce compound **1**. The subsequent addition of CO to a solution of **5** resulted in its complete conversion to complexes **1** and **2**, thus confirming that it does react with free CO in this manner.
The fate of the DMAD ligand in this reaction remains undetermined. It is possible that hydrogenation of the coordinated alkyne to either dimethyl fumarate or dimethyl maleate may take place but we have found no ^1H NMR evidence to suggest such an event. The fact that compound **5** can also be prepared from *trans*-$[RhCl(CO)(dmpm)]_2$ indicates that the presence of DMAD in the reactant is not necessary to the outcome.

In contrast to the above results, the HFB complex, **4**, showed little tendency to react with $NaBH_4$ or $LiBEt_3H$. The $^{31}P\{^1H\}$ NMR spectrum of a mixture of $[Rh_2(CO)_2(\mu\text{-}HFB)(dmpm)_2]/NaBH_4$ did show the presence of a single new unsymmetrical species after three days under H_2, however, this new product was present only in very low concentrations and we were unable to characterize it further. A solution of **4** was deliberately exposed to air to see if this new species was simply an air oxidation product. Numerous resonances appeared in the $^{31}P\{^1H\}$ NMR spectrum of the sample but none of these corresponded to those of the compound in question.

In the ^{11}B NMR spectrum of complex **5** a broad quintet is observed at δ -18.0 ($^1J_{B-H}$= 87 Hz). The magnitude of B-H coupling is similar to that reported for other BH_4^- containing complexes [40,41] and to $NaBH_4$ itself (δ -40.0 in THF-d_8, $^1J_{B-H}$= 82 Hz).[54] The appearance of a quintet indicates the boron unit to be BH_4^- and implies the equivalence of all four protons associated with boron. Proton-decoupling the signal results in a singlet which broadens into the baseline upon cooling, presumably due to the spin-lattice relaxation of the ^{11}B and ^{10}B nuclei.[43,47,52,54] Consequently we were unable to observe a fully resolved boron resonance. The presence of only one "BH_4" unit per molecule was established by the careful addition of a known amount of $BF_3 \cdot OEt_2$ to the NMR sample tube and integration of the new resonance, a singlet (δ 0.0 ppm) due to BF_3, against that of "BH_4". Thus, the formation of a species such as $[Rh(BH_4)H(dmpm)]_2$, similar in nature to $[V(\eta^2\text{-}BH_4)(\mu\text{-}Cl)(dmpm)]_2$[46b] or the proposed species $[V(\eta^2\text{-}BH_4)(\mu\text{-}H)(PMe_3)_2]_2$,[45b] seems unlikely. The realization of only one boron unit in complex **5** necessitates the presence of an additional ligand in the complex in order to avoid an unrealistic, coordinatively-unsaturated complex. A hydride ligand is proposed in Scheme 4.1. Subsequent reaction of compound **5** with CO to provide $[Rh_2(CO)_3\text{-}(dmpm)_2]$ (**1**) could then be rationalized by the loss of H_2 and $1/2B_2H_6$.

Evidence for the presence of a hydride ligand in compound **5** appears in the room temperature ^{1}H NMR spectrum, which contains two very broad featureless resonances at δ -1.1 ppm and δ -1.7 ppm. These resonances have been collectively assigned to the "BH_4^-" and hydride ligands. Individually they integrate as ca. 1:1 and together they consistently integrate as five protons relative to the methylene (four protons) and the methyl protons (twenty-four protons) of dmpm. The poor resolution of these hydride resonances is typical of coordinated BH_4^- and most likely stems from a combination of the quadrupole effect of ^{11}B and ^{10}B,[43,47,52,54] and rapid exchange of bridge and terminal protons.

Assuming that a metal-hydride ligand is present in complex **5**, we propose that, in addition to bridge-terminal B-H exchange at a single metal centre, "BH_4^-" undergoes intramolecular migration between metal centres by the transfer of "BH_3" from one metal-hydride to the other. Such rapid movement could reasonably be expected to produce a symmetrically averaged ^{31}P{^{1}H} NMR signal like the AA'A"A"'XX' pattern which is actually observed. Rapid, intramolecular migration of BH_4^- has also been proposed by Fryzuk and coworkers for the binuclear hafnium complex $[Hf(N(SiMe_2CH_2PMe_2)_2)]_2(\mu\text{-}H)(BH_4)$.[41] Although an intermolecular



5

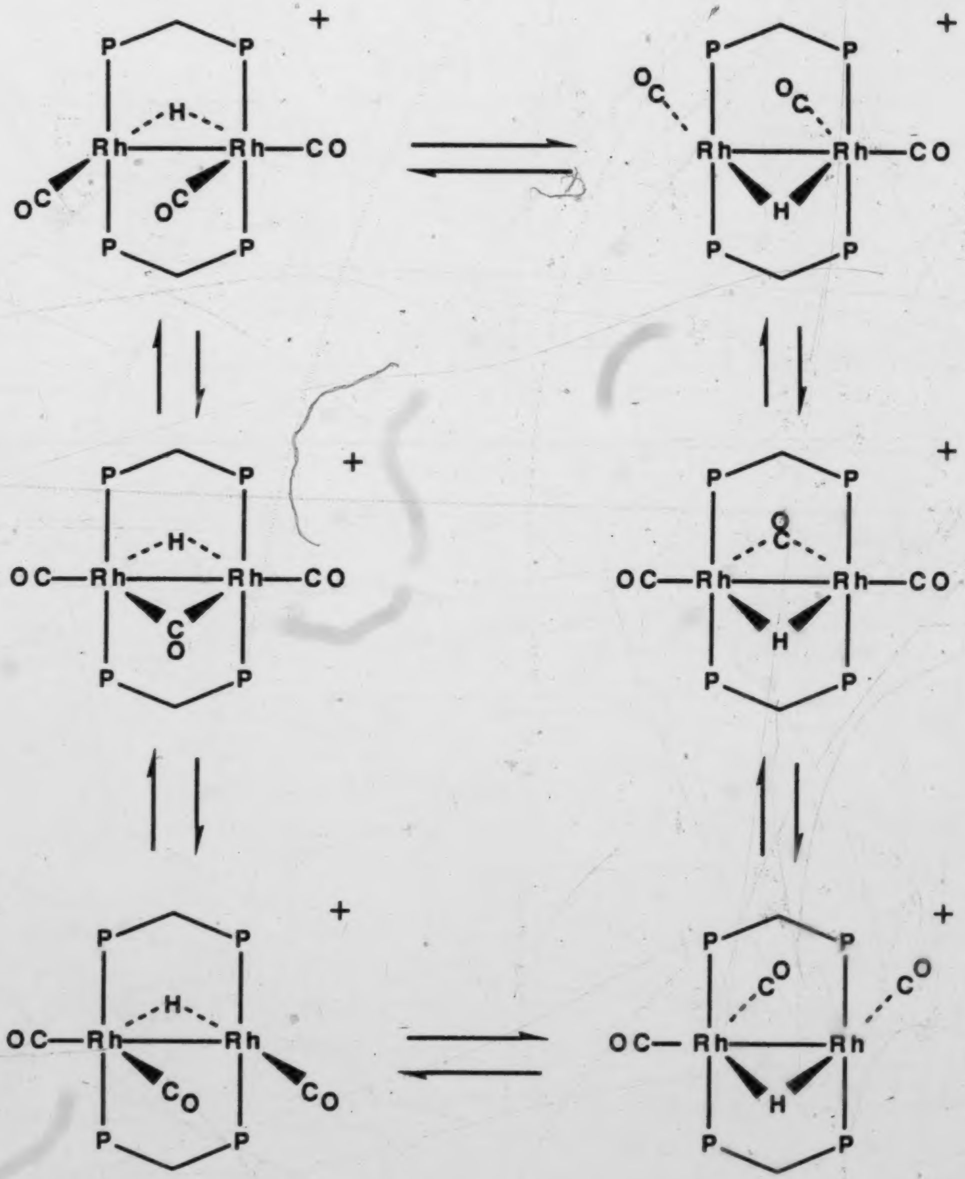
process cannot be ruled out, the possibility that the "BH_4^-" unit of **5** is involved in an equilibrium with free BH_4^- ion seems unlikely. This conclusion is based on the fact that the addition of solid $NaBH_4$ to a sample of **5** resulted in the appearance of a resolved four-line pattern at δ -0.53 (THF-d_8) in the ^{1}H NMR spectrum and no apparent increase in intensity of the two unresolved resonances due to coordinated BH_4^- and the proposed hydride ligand. As well, conductivity measurements on the original solution do indicate a small conductance (acetonitrile, $\Lambda(10^{-3}\text{ M}) = 33\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$) but it is much less than normal 1:1 electrolyte values ($\Lambda(10^{-3}\text{ M}) = 120\text{-}160\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$) in acetonitrile.[6] The observed conductivity is likely due to a small amount of NaCl impurity remaining from the original chloride removal reaction.

Low temperature NMR studies of $[Rh_2(BH_4)(H)(\mu\text{-}CO)(dmpm)_2]$ (**5**) were carried out in an effort to confirm the proposed configuration of the molecule and to obtain a clearer picture of the fluxional process taking place. Although the $^{31}P\{^1H\}$ NMR spectrum of compound **5** does not change over the range of temperatures studied (25° to -90°C), the ^{1}H NMR spectrum does. As the temperature is lowered the BH_4^- resonances of **5** collapse into the baseline and eventually reappear (-85°C) at δ -3.55 and δ -5.20. They are now much more prominent in the spectrum but both are still essentially featureless and do not provide any further insight into the spin-spin coupling or the mode of BH_4^- coordination. Boron-decoupling the spectrum has a marginal effect on the resonances, transforming the lowerfield one into a very broad, unresolved doublet. This may possibly indicate the separation of bridging and terminal BH_4^- proton resonances but this cannot be stated with confidence. Since the corresponding $^{31}P\{^1H\}$ NMR spectrum does not change over the temperature range 25 to -85°C we must attribute the lack of resolution in the proton spectrum primarily to the fluxionality of the molecule. Unfortunately this has made it impossible to distinguish between separate M-BH_4 and M-H resonances.

In the absence of X-ray structural data, infrared spectroscopy has generally been a useful tool for determining the mode of BH_4^- coordination.[43,55] However, due to a complicated infrared spectrum there is no clear indication of this mode in complex 5. Bands attributed to the BH_4^- moiety are observed at 2387 cm^{-1}, 2364 cm^{-1} and 1147 cm^{-1}. The first two appear as a doublet and are assigned to the boron terminal-hydride stretch, suggesting η^1-BH_4^- coordination ($\upsilon(B\text{-}H_t)$= a doublet between 2300-2450 cm^{-1} for η^1-BH_4^- coordination).[43] The band at 1147 cm^{-1} is assigned to a deformation (either BH_2, 1100-1200 cm^{-1} or BH_3, 1000-1150 cm^{-1}). In the infrared spectrum of the deuterium substituted analogue, $[Rh_2(BD_4)D(\mu\text{-}CO)(dmpm)_2]$, the BD_4^- bands appear at 1800 cm^{-1} (a broad singlet) and 860 cm^{-1} (deformation band). The calculated υ_H/υ_D ratio of 1.33 is within the range (1.30 to 1.35) found for other complexes which contain BH_4^-.[42,45,48] Additional M-BH_4 or M-BD_4 bands as previously reported[43] ($\nu(M\text{-}H_b)$= 2000-1700 cm^{-1}, $\nu(B\text{-}H_b)$~ 2000 cm^{-1} for η^1 ; bridge stretch = 1300-1500 cm^{-1}, $\nu(B\text{-}H_b)$= 1650-2150 cm^{-1} for η^2 coordination, b= bridging) were either not present in the spectrum or they were overlapped by bands associated with other parts of the molecule. The situation was complicated somewhat by the occurrence of bands due to $[Rh_2(CO)_3(dmpm)_2]$ (see Table 4.1).

(b) Reaction of reduced complexes with HBF_4•OEt_2. The compound $[Rh_2(CO)_3(dmpm)_2]$ (**1**) adds one equiv of HBF_4•OEt_2 in solution to yield the hydride-bridged species $[Rh_2(CO)_3(\mu\text{-}H)(dmpm)_2][BF_4]$ (**6**). The solution-infrared spectrum of compound **6** contains three bands in the carbonyl region (ν(CO)= 1980 (m, sh), 1960 (vs) and 1895 (w) cm^{-1}, THF). The $^{31}P\{^1H\}$ NMR spectrum of the complex, an AA'A"A'''XX' spin pattern both at room temperature (δ 6.49) and -85°C, is consistent with a symmetrical species. However, the appearance of only one resonance in the carbonyl region of the $^{13}C\{^1H\}$ NMR spectrum (a singlet at δ 194.1) shows that the molecule is highly fluxional and that all three carbonyl ligands are equilibrated. The fluxional behaviour of **6** is characteristic of "$Rh_2(dmpm)_2$" chemistry but contrasts that observed for the homobimetallic-dppm analogues, $[Rh_2(CO)_2(\mu\text{-}H)(\mu\text{-}CO)(dppm)_2]^+$ [10a,b] and $[Ir_2(CO)_2(\mu\text{-}H)(\mu\text{-}CO)(dppm)_2]^+$,[8] both of which have symmetrical A-frame structures involving the hydride and a carbonyl ligand fixed in bridged positions. For the case at hand, we propose the fluxional process illustrated in Scheme 4.2. As shown, the complete exchange of carbonyl ligands must involve their movement in and out of a bridged position from one metal to the other. This requires the formation of an "all terminal CO" species, the type of which has been postulated for the heterobimetallic complexes $[RhIr(CO)_3(\mu\text{-}H)(dppm)_2][BF_4]$,[4] $[RhFe(CO)_3(\mu\text{-}H)(dppm)_2]$ [12] and $[CoRh(CO)_3(\mu\text{-}H)(dppm)]^+$.[13] At low temperature (-85°C) the $^{13}C\{^1H\}$ NMR spectrum of **6** now indicates the presence of a bridging carbonyl species with a resonance at δ 196.4 (triplet of quintets, $^1J_{C\text{-}Rh}$= 34.1 Hz, $^2J_{C\text{-}P}$= 7.4 Hz). An additional resonance, appearing at δ 188.3 (unresolved multiplet),

Scheme 4.2

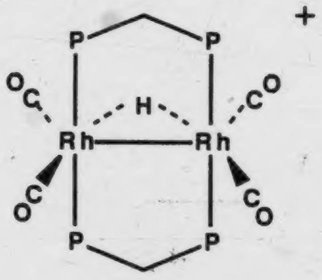


is tentatively assigned to the terminal carbonyl ligands of the bridging-CO species. The fact that this latter resonance is essentially unresolved and that both the low temperature (-85°C) $^{31}P\{^1H\}$ and ^1H (vide infra) NMR spectra do not differ significantly from those taken at room temperature suggest that the molecule is still fluxional at this temperature.

Terminal carbonyl exchange on the same metal of compound **6** most likely takes place in a manner which is similar to that proposed for the heterobimetallic examples listed above, as well as the related homonuclear diiridium system,[56] via tunneling of the hydride ligand through the metal-metal vector. The exchange of CO between the metal-centres of **6** must occur by formation of a symmetrical carbonyl-bridged species. It is interesting to note that complete CO exchange between metal centres is not observed for the heterobimetallic complexes, presumably because of the greater preference of one metal for the additional CO ligand and the 18 electron configuration that results in this 16-18 electron species.

The room temperature ^1H NMR spectrum of **6** contains a resonance (δ -9.34) consisting of a nine line pattern (an overlapped triplet of quintets) which is assigned to the metal-hydride ligand. Upon phosphorus-decoupling the spectrum the resonance transforms into a triplet ($^1J_{H\text{-}Rh}$= 25.2 Hz, $^2J_{H\text{-}P}$= 11.5 Hz) showing that the hydride is coordinated to both rhodium atoms. There is very little change in this resonance at low temperature (-85°C) and although we cannot entirely rule out other forms of exchange involving a terminal hydride species, there is no evidence to suggest that the hydride ligand moves out of the bridged position. This has also been the conclusion for the mixed-metal dppm complexes.[4,12] As mentioned earlier, the appearance at -85°C of a single resonance each for the methylene and methyl protons (see Table 4.2) of dmpm indicates that the molecule is fluxional at this temperature.

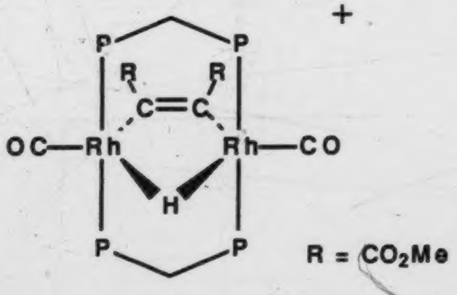
Complex **6** adds one equiv of CO to yield the tetracarbonyl species $[Rh_2(CO)_4(\mu\text{-}H)(dmpm)_4][BF_4]$ (**7**). Based on spectroscopic evidence we propose the geometry for compound **7**, illustrated below, which is analogous to that proposed for the related hydride species $[Ir_2(CO)_4(\mu\text{-}H)\text{-}(dppm)_2][BF_4]$.[57] The preparation of compound **7** follows the trend of "$Rh_2(dmpm)_2$" complexes in forming products containing a higher number of CO ligands than their "$Rh_2(dppm)_2$" counterparts (see the discussion of $[Rh_2Cl(CO)_3(\mu\text{-}CO)(dmpm)_2][BF_4]$ and $[Rh_2(CO)_4(\mu\text{-}S)(dmpm)_2]$ in Chapter 2). Like these other "$Rh_2(dmpm)_2$" complexes, compound **7** is quite labile and readily loses CO under N_2 to provide the tricarbonyl starting material **6**.



7

Consistent with the proposed geometry, only terminal CO stretches are revealed in the solution infrared spectrum ($\nu(CO) = 1985\ cm^{-1}$, $1958\ cm^{-1}$). The $^{31}P\{^1H\}$ NMR spectrum resembles the typical second-order AA'A"A"'XX' pattern of a symmetrical complex both at room and low temperature (δ 1.93, -40°C, see Table 4.2). In the ^{1}H NMR spectrum (-40°C) of **7**, the hydride resonance appears as a complex nine line pattern (δ -7.65). The multiplet is transformed into a triplet upon phosphorus-decoupling the spectrum, thus confirming that the hydride is bridged between the two metal atoms ($^1J_{H-Rh}$= 21.9 Hz, $^2J_{H-P}$= 11.5 Hz). The appearance of only one resonance each for the methylene (δ 3.32) and methyl (δ 1.78) protons points to a fluxional molecule whereby the bridging hydride ligand is tunneling through the metal-metal vector as in the tricarbonyl example. Consistent with this proposal, a single complex resonance consisting of a doublet of multiplets appears in the carbonyl region of the $^{13}C\{^1H\}$ NMR (δ 199.4, -40°C) indicating that all four carbonyl ligands are equilibrated.

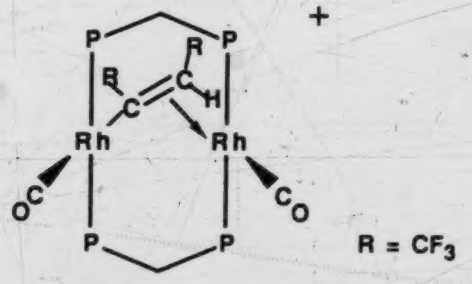
The addition of HBF_4•OEt_2 to the alkyne complexes **3** and **4** was expected to produce stable metal-hydride derivatives which could be more easily characterized than the neutral starting materials. However, neither species is very stable, especially $[Rh_2(CO)_2(\mu\text{-DMAD})(\mu\text{-H})(dmpm)_2][BF_4]$ (**8**), the major product of HBF_4•OEt_2 addition to complex **3**. Spectroscopic investigations of the reaction mixture indicate compound **8** to be of the form illustrated below. The complex is symmetrical about the two



8

rhodium atoms as evidenced by the AA'A"A'"XX' spin-spin pattern observed in the $^{31}P\{^1H\}$ NMR spectrum (δ -4.2). The terminally bound CO ligands appear at 1988 cm^{-1} and 1974 cm^{-1} and the carboxylate CO group of DMAD at 1743 cm^{-1} in the solution-infrared spectrum (THF). A complex metal-hydride resonance consisting of nine lines appears in the ^1H NMR spectrum of complex **8** at δ -11.53 ppm. Upon phosphorus-decoupling the spectrum the resonance is transformed into a triplet ($^1J_{H\text{-}Rh}$= 22.5 Hz), indicating a bridging metal-hydride ligand. Like the other Rh-H complexes (**6** and **7**) reported in this chapter, compound **8** was found to decompose in solution with time or upon addition of hexane or diethyl ether and was not successfully isolated as a solid.

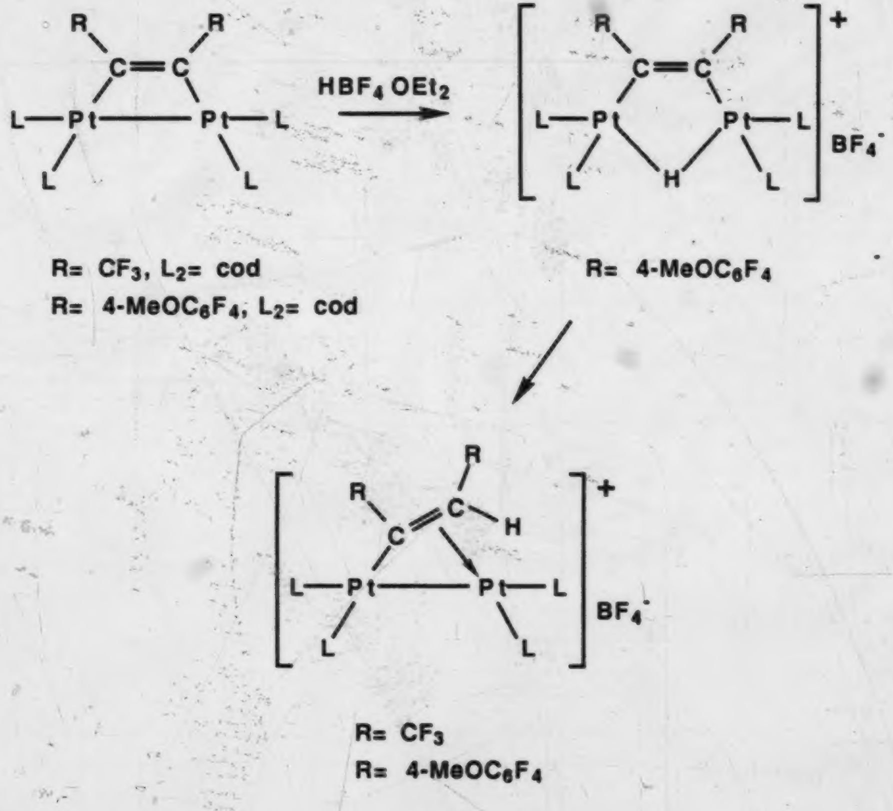
The reaction of $[Rh_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ (**4**) with one equiv of $HBF_4{\bullet}OEt_2$ also yields an unstable species, $[Rh_2(CO)_2(F_3CC{=}C(H)CF_3)(dmpm)_2][BF_4]$ (**9**), but one in which H^+ has combined with the alkyne to form a vinylic ligand. The general lack of resolution in all NMR spectra of complex **9** suggests that the molecule is fluxional ($^{31}P\{^1H\}$, δ -0.5, multiplet, see Table 4.2). At room temperature the vinylic proton is apparent in the ^1H NMR as a broad resonance at δ 5.85 and the fluorine atoms of the two



9

CF_3 groups appear at δ -51.7 and δ -59.9 in the ^{19}F NMR spectrum. Neither spectra provide H-F or F-F coupling data, however, we know from the subsequent reaction of compound **9** with CO and characterization of the tetracarbonyl product, $[Rh_2(CO)_3(\mu\text{-}CO)\text{-}(F_3CC{=}C(H)CF_3)(dmpm)_2][BF_4]$ (**10**) discussed below, that the two CF_3 groups occupy cis positions across the double bond of the vinylic moiety. Studies of the carbonyl region of the $^{13}C\{^1H\}$ NMR spectrum have revealed that both carbonyl ligands of **9** remain terminally bound (δ 196.14, $^1J_{C\text{-}Rh}$= 50 Hz; δ 179.03, $^1J_{C\text{-}Rh}$= 74 Hz. at -85°C). The proposed geometry of **9** requires a σ, π interaction of the vinylic ligand as shown, to maintain a 16-electron configuration at the metal centres. This proposed interaction is not unlike that which is observed in the acetylide-bridged species $[Rh_2(CO)_2(\mu\text{-}C_2\text{-}t\text{-}Bu)(dppm)_2][ClO_4]$ [58] and that which is reported for $[Pt_2(F_3CC{=}C(H)CF_3)(cod)_2][BF_4]$ [34] and suggested for $[(\eta^5\text{-}C_5H_5)_2Rh_2(F_3CC{=}C(H)CF_3)(CO)_2][BF_4]$.[59]

As in most examples of protic-acid addition to metal-coordinated HFB complexes, it is not clear in the above case whether protonation of the starting material occurs initially at a metal centre or directly at the alkyne ligand.[59-62] Evidence for the presence of small amounts of reaction by-products (involving M-H resonances) are observed in the ^1H NMR spectrum of compound **9** but due to the nature of the reaction-mixture workup it is difficult to determine whether any intermediate M-H complexes were actually formed. Based on the observation that the DMAD analogue **8** has the hydride ligand bridging both metals, it is proposed that H^+ addition to $[Rh_2(CO)_2(\mu\text{-}HFB)(dmpm)_2]$ (**4**) yields an analogous metal-hydride species which subsequently rearranges to the vinylic product **9**. A similar reaction sequence (illustrated below) involving the addition of $HBF_4 \cdot OEt_2$ to the diplatinum complex $[Pt_2(\mu\text{-alkyne})(cod)_2]$ has been reported by Stone and coworkers.[34] It was found that when the alkyne was HFB, only a cationic vinyl-bridged complex was detected. When the alkyne was $C_2(4\text{-}MeOC_6F_4)_2$, an initial hydride-bridged alkyne-bridged species,

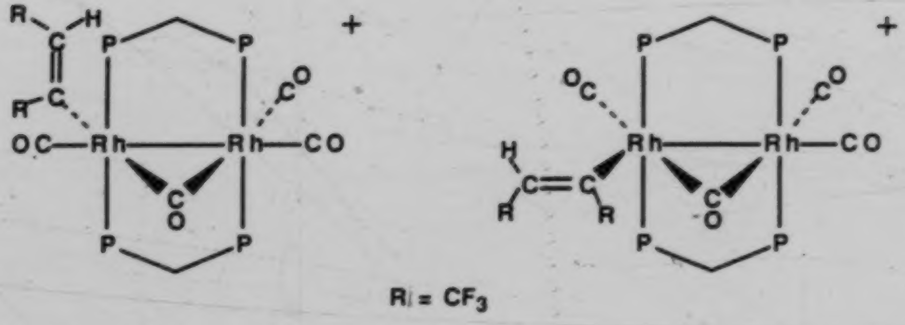


similar to complex 8, was formed which subsequently rearranged to a vinyl compound. We favour a similar reaction pathway for the formation of complex 4 and suggest that under the proper reaction conditions it may be possible to induce the DMAD species 8 to form a vinylic complex as well. Our initial investigation into this matter has revealed that an unsymmetrical species does form, however, its characterization has remained incomplete due to the complexity of the reaction mixture.

Although we favour the process involving the initial coordination of H^+ to a metal centre of compound **4**, we cannot rule out the possibility of direct alkyne protonation; $M_{\delta+}$-$C_{\delta-}$ bond polarization,[63] brought about by electron withdrawing groups on the alkyne,[60,61] may make the alkyne carbon atom the most likely site of electrophilic H^+ attack. The differences in electron withdrawing ability between HFB and DMAD [64] may explain why the reactions of complexes **3** and **4** with acid produce different results. At present, the information is insufficient to make any conclusive statements regarding such a mechanism.

Exposure of compound **9** to CO in THF solution affords the tetracarbonyl species $[Rh_2(CO)_3(\mu\text{-}CO)(F_3CC{=}C(H)CF_3)(dmpm)_2][BF_4]$ (**10**) as a bright yellow precipitate. The product is stable in solution (CO saturated) and solid form when under an atmosphere of CO, but readily loses CO under N_2 to provide a number of as yet uncharacterized species. Thus, we were unable to characterize the intermediate tricarbonyl species. The $^{31}P\{^1H\}$ NMR spectrum of complex **10** at room temperature is partially unresolved but at -40°C a pattern consisting of two sets of pseudotriplets (δ 6.12, 3.50), typical of an AA'BB'XY spin-system, is observed. In the ^1H NMR spectrum the vinylic proton resonance now appears as a quartet (δ 6.10 ppm, $^3J_{H\text{-}F}$ [illegible] 10 Hz) due to coupling with the three fluorine atoms of the geminal CF_3 group.[65 71] In low temperature (-40°C) ^{19}F NMR studies the two CF_3 resonances appear at δ -51.48 (quartet, $^5J_{F\text{-}F}$= 12.2 Hz) and δ -59.36 (a doublet of quartets, $^5J_{F\text{-}F}$= 12.2 Hz, $^3J_{F\text{-}H}$= 10 Hz). The second resonance has a more complex splitting pattern due to F-H coupling and therefore is assigned to the CF_3 group located geminal to the proton. Upon proton decoupling the spectrum, this resonance becomes a quartet as only the F-F interaction remains. The magnitude of $^5J_{F\text{-}F}$ indicates a relative cis disposition of the CF_3 groups (trans CF_3's exhibit $^5J_{F\text{-}F}$~ 2-3 Hz; cis CF_3's exhibit $^5J_{F\text{-}F}$ ~ 12-15 Hz).[65-71] The cis geometry is consistent with all other reported H^+ additions to metal coordinated HFB.[34,59-61,63]

Evidence for the four carbonyl ligands of compound **10** is found in the infrared spectrum which contains three terminal bands at 2044, 2014 and 1988 cm^{-1} and a single bridging carbonyl band at 1765 cm^{-1}. The carbonyl region of the $^{13}C\{^1H\}$ NMR spectrum also confirms the presence of four carbonyl ligands with resonances appearing at δ 234.6, δ 199.0, δ 198.1 and δ 190.8 ppm (-40°C in THF-d_8). We had hoped to use $^{13}C\{^1H\}$ NMR data to assign the configuration of the CO ligands in the molecule but due to numerous spin-spin coupling sources all resonances in this region appear as complex multiplets. The coupling interactions have therefore been difficult to interpret and we were unable to distinguish between two isomers, **E** and **F**, in which the bridged carbonyl ligand is trans or cis to the vinylic moiety, respectively. In the CO region of the $^{13}C\{^1H\}$ NMR spectrum the highest-field resonance (δ 190.8) is the least complicated and can be assigned to the carbon atom of the lone terminal CO on rhodium. Appearing as a doublet of quartets, it is actually an overlapped doublet ($^1J_{C\text{-}Rh}$= 69.1 Hz) of doublet (12 Hz) of triplets ($^2J_{C\text{-}P}$~ 14 Hz). Upon broadband phosphorus-decoupling the sample, the pattern is



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simplified into a doublet of doublets. It is not clear from the decoupling experiments whether the coupling of 12 Hz arises from either a two-bond C-C interaction with a trans-oriented, bridged-CO ligand as in **F** (see Chapter 6 for a discussion on the magnitude of this type of coupling) or a two-bond interaction with the second rhodium via the metal-metal bond as in **E**. The complex lowfield-resonance (δ 234.6) is assigned to the carbon atom of the bridging carbonyl ligand. It is simplified into a five line pattern resembling an overlapped doublet of doublet of doublets (in the phosphorus-decoupled spectrum) but no coupling information was obtained; in particular it was not possible to confirm or reject the earlier proposal of 12 Hz coupling between trans carbonyl ligands. Although the remaining two resonances (δ 199.0, 198.1) have been assigned to the carbon atoms of the terminally coordinated CO ligands, the complex nature of the signals has made individual assignments impossible.

Attempts to oxidatively add organic fragments (acetyl chloride) to the reduced species $[Rh_2(CO)_3(dmpm)_2]$ (**1**), $[Rh_2(CO)_2(\mu\text{-DMAD})(dmpm)_2]$

(3) or [$Rh_2(CO)_2(\mu$-HFB)(dmpm$)_2$] (4) has, for the most part, resulted in the reformation of the chloride precursors. One exception involves the reaction of complex 4 with acetyl chloride to yield, in addition to the dichloride starting material [$Rh_2Cl_2(CO)_2(\mu$-HFB)(dmpm$)_2$], a new species which apparently has the acetyl fragment incorporated in it. The complex has not been completely characterized but the $^{31}P\{^1H\}$ NMR resonances (δ -3.28, a doublet of pseudotriplets with 121 and 21 Hz separation between the peaks; δ -8.24, a doublet of pseudotriplets with 122 and 21 Hz separation between the peaks) show it to be unsymmetrical in nature. The presence of an acetyl group in the complex is evident from the solid-state and solution infrared spectra, both of which contain a single band due to the acyl carbonyl at 1660 cm^{-1} (Nujol) and 1666 cm^{-1} (THF), respectively. A terminal metal-carbonyl stretch also appears at 1981 cm^{-1} in both spectra. The dichloride species, [$Rh_2Cl_2(CO)_2(\mu$-HFB)(dmpm$)_2$] is observed as a minor product at 2031 cm^{-1} (Nujol). Obviously a more complete characterization of the new complex is in order but we speculate that the addition has occurred with the coordination of both the chloride and acetyl fragment to a single metal centre.

Conclusions

The chemical reduction of the complexes *trans*-[RhCl(CO)(dmpm)$]_2$ (under CO), [$Rh_2Cl_2(CO)_2(\mu$-DMAD)(dmpm$)_2$] and [$Rh_2Cl_2(CO)_2(\mu$-HFB)-(dmpm$)_2$] yielded the highly reactive species [$Rh_2(CO)_3$(dmpm$)_2$] (1), [$Rh_2(CO)_2(\mu$-DMAD)(dmpm$)_2$] (3) and [$Rh_2(CO)_2(\mu$-HFB)(dmpm$)_2$] (4), respectively. The structures of these three complexes, as well as the majority of other compounds reported in this chapter are based on the geometry of complexes found in the related hetero- and homo-bimetallic-dppm systems. For example, the species $[Rh_2(CO)_3(dmpm)_2]$ appears to be very closely related to its direct dppm analogues, $[Rh_2(CO)_3(dppm)_2]$,[10] $[CoRh(CO)_3(dppm)_2]$ [12,13] $[RhIr(CO)_3(dppm)_2]$ [4] and $[Ir_2(CO)_3(dppm)_2]$ [8] and to its diiridium analogue, $[Ir_2(CO)_3(dmpm)_2]$,[5] possessing a somewhat unusual unsymmetrical structure with a 16-18 electron configuration and a dative bond between the metal centres. The curious borohydride complex $[Rh_2(BH_4)H(\mu\text{-}CO)(dmpm)_2]$ (5) has no direct dppm analogue but it does appear to have a typical bimetallic-diphosphine A-frame type structure.

As in Chapter 2, we see further evidence to suggest that the basicity and the size of the dmpm ligand strongly affect the chemical reactivity of binuclear-rhodium complexes. The highly reactive nature of all "$Rh_2(dmpm)_2$" species prepared in this chapter is evident from their rapid decomposition in the presence of air. In contrast, the majority of dirhodium analogues are air sensitive to a much lesser extent and so for example $[Rh_2(CO)_3(dppm)_2]$,[10] $[RhIr(CO)_3(dppm)_2]$,[4] $[Ir_2(CO)_3(dppm)_2]$ [8] and $[Ir_2(CO)_2(\mu\text{-}DMAD)(dppm)_2]$ [33] can all be manipulated in air for short periods of time without the occurrence of significant decomposition. Unlike their dppm counterparts, the reduced "$Rh_2(dmpm)_2$" species $[Rh_2(CO)_3(dmpm)_2]$ (1), $[Rh_2(CO)_2(\mu\text{-}DMAD)(dmpm)_2]$ (3) and $[Rh_2(CO)_2(\mu\text{-}HFB)(dmpm)_2]$ (4) quickly revert to their respective starting materials upon exposure to chlorinated solvents. The remaining "$Rh_2(dmpm)_2$" compounds in this chapter react with chlorinated solvents as well, providing a number of uncharacterized species. This behaviour has made it difficult to study the oxidative-addition of any organic reagents (such as acetyl chloride) which contain a halide.

It now appears from the investigations made in this chapter that the small size of the dmpm ligand has a much greater effect on ligand rearrangement and the reactivity of the complex than was originally suspected (Chapter 2). In this regard, variable temperature NMR studies have shown virtually all the complexes in this chapter to have some degree of fluxionality. This behaviour is perhaps not that surprising in some cases since reactions such as the reduction of *trans*-$[RhCl(CO)(dmpm)]_2$ under CO have provided species ($[Rh_2(CO)_3(dmpm)_2]$) which, on comparison with their dppm analogues, could be predicted to be highly fluxional. On the other hand, complexes such as $[Rh_2(CO)_3(\mu\text{-}H)(dmpm)_2][BF_4]$ undergo complete M-CO rearrangement whereas the analogous dppm-bridged species, $[Rh_2(CO)_2(\mu\text{-}H)(\mu\text{-}CO)(dppm)_2]^+$ [10a] and $[Ir_2(CO)_2(\mu\text{-}H)(\mu\text{-}CO)(dppm)_2]^+$ [8] are not fluxional. We therefore attribute the relative ease with which most of the "$Rh_2(dmpm)_2$" species decompose in solution or transform into numerous (uncharacterized) complexes to the small size of the dmpm ligands.

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Chapter 5

Binuclear Bis(alkyne) Complexes of Rhodium

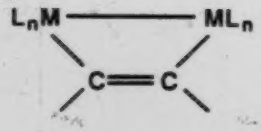
Introduction

Interest in alkyne-metal complexes stems from the desire to modify the reactivity of alkynes by complexation with a metal centre and subsequently provide new synthetic routes to organic products. A variety of alkyne transformations on mononuclear metal complexes are possible, such as alkyne dimerization, trimerization, higher order polymerization and oxidative coupling.[1-6] Alkyne transformations on two adjacent metal centres are also of great interest in light of suggestions made concerning the involvement of two metal atoms in catalytic alkyne coupling reactions.[7]

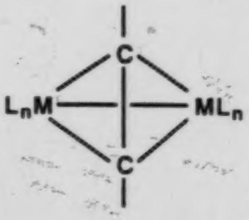
Binuclear complexes have already proven useful in the formation of C-C bonds via the interaction of alkyne molecules with organic fragments, including other alkynes and alkylidenes.[7-11] It is anticipated that the further study of these systems may lead to forms of alkyne reactivity which have not been realized in mononuclear systems. This chapter focuses on the reactivity of electron-rich "$Rh_2(dmpm)_2$" compounds in the presence of electrophilic alkyne molecules in an attempt to broaden the scope of alkyne reactivity with binuclear diphosphine complexes.

The reaction of alkyne molecules with binuclear transition-metal complexes which are bridged by diphosphine or related ligands (dppm,[12,13a-13d,14-17] dpam (bis(diphenylarsino)methane),[13a] Ph_2Ppy

(2-pyridyldiphenylphosphine),[13e] and ETM (bis(ethylthio)methane)[10]) often results in the incorporation of an alkyne molecule in a bridged fashion between the two metals. Terminal coordination is much less common.[18] Bridging alkyne ligands can adopt two possible bonding modes, coordinated either parallel to the metal-metal axis as a cis-dimetalated olefin, **A**, or perpendicular to the metal-metal axis as a tetrahedral form, **B**.[19] The former mode predominates in diphosphine-bridged complexes.[12a-12f,13a-13d,14,15,17] although examples of type **B** have also been reported [12g,16] and interconversion of **A** to **B** is known to take place.[12g,16a] In general though, once coordinated in the bridging fashion, the alkyne unit shows little tendency for bridge rearrangement or subsequent reaction with other ligands on the complex.[12f,20] Exceptions to this trend include the complexes [$Pd_2X_2(\mu\text{-DMAD})(dppm)_2$] (X= Cl or I),[15] both of which appear to behave as catalyst precursors for the cyclotrimerization of alkynes. Based on crossover experiments, these reactions imply the formation of intermediates in which alkyne molecules have been combined on the metal. Apart from the cyclotrimerization product, however, only monoalkyne species have been recovered from these reactions.



A



B

Presumably the poor lability of the alkyne unit in binuclear diphosphine-bridged compounds can be attributed to a strong metal-alkyne interaction brought about by π-backbonding from the metal atoms to the π^* orbital of the alkyne carbon atoms. Although compounds with electron-rich metal centres would be expected to heighten the potential for strong metal-alkyne interactions there should also be a better chance of coordinating more than one alkyne molecule and possibly combining the two, provided the original complex is coordinatively unsaturated. The coordination of two alkyne ligands in the complex has been proposed as a key step in alkyne cyclisation reactions.[3,6,7]

Given the propensity of the electron rich complexes $[Rh_2(CO)_3(dmpm)_2]$, $[Rh_2(CO)_2(\mu\text{-DMAD})(dmpm)_2]$ and $[Rh_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ to undergo oxidative addition of electrophilic reagents such as $HBF_4{\bullet}OEt_2$ and HCl (Chapter 4), it was speculated that their reactivity with the electrophilic DMAD and HFB molecules would provide an opportunity to study new alkyne complexes in which more than one alkyne molecule is coordinated to the metals. Ultimately, these compounds may provide further details on the type of intermediates which are involved in the combination reactions of alkynes, such as cyclotrimerization.

Experimental Section

General comments. Experimental conditions are as described in Chapter 2. Dimethyl acetylenedicarboxylate (DMAD), diphenylacetylene, dimethylacetylene and tetrafluoroboric acid etherate ($HBF_4{\bullet}OEt_2$) were obtained from The Aldrich Chemical Company. Carbon monoxide, (C. P., grade) was purchased from Matheson, ^{13}CO (99%) from Isotec Inc. and hexafluoro-2-butyne (HFB) from SCM Speciality Chemicals. These and all other reagent grade chemicals were used as received. $[Rh_2(CO)_3(dmpm)_2]$, $[Rh_2(CO)_2(\mu\text{-DMAD})(dmpm)_2]$ and $[Rh_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ were prepared by the procedures reported in Chapter 4. All physical measurements were carried out as described previously in Chapter 2 and all spectroscopic data are recorded in Tables 5.1 and 5.2.

Preparation of Compounds. (a) $[Rh(CO)(\mu\text{-DMAD})(dmpm)]_2$ (1). Method A. A purple solution of $[Rh_2(CO)_2(\mu\text{-DMAD})(dmpm)_2]$ (0.100 mmol based on 75% conversion of 100 mg, 0.134 mmol of $[Rh_2Cl_2(CO)_2\text{-}(\mu\text{-DMAD})(dmpm)_2]$) in THF (8 mL) was prepared as reported in Chapter 4. One equiv of DMAD (12.5 μL, 0.100 mmol) was added and the mixture stirred for 1 h. The brown THF solution was removed by cannula under positive N_2 pressure. The resulting yellow solid was recrystallized from CH_2Cl_2/hexane and dried under vacuum. Compound **1** was obtained as a yellow powder in 38% yield (41 mg). The product was partially soluble in hexane and the recrystallization solution had to be cooled to 0°C to effect complete precipitation of the solid. Anal. Calcd for $C_{24}H_{40}O_{10}P_4Rh_2$: C, 35.2%; H, 4.9%. Found: C, 34.7%; H, 4.9%.

Method B. An orange solution of $[Rh_2(CO)_3(dmpm)_2]$ in THF (5 mL) was prepared as described in Chapter 4 using *trans*-$[RhCl(CO)(dmpm)]_2$ (50 mg, 0.083 mmol). Three equiv of DMAD (30 μL, 0.25 mmol based on 100% conversion of the starting material) were added to the solution, producing an immediate colour change from orange to purple and then brown. This was followed soon thereafter by the precipitation of a brown-yellow solid.

Table 5.1. **Infrared Spectroscopic Data for the Compounds in Chapter 5.**[a]

no.	compound	Nujol, cm^{-1}		CH_2Cl_2 solution, cm^{-1}	
		ν(CO)	ν(CC)	ν(CO)	ν(CC)
1	$[Rh(CO)(\mu\text{-DMAD})(dmpm)]_2$	1962(s), 1670(s),^{b} 1649(s)^b	1526(m)	1964(s), 1670(m)^b	1525(w)
2	$[Rh_2(CO)_2(\mu\text{-DMAD})(\mu\text{-HFB})(dmpm)_2]$	1967(s), 1672(m),^{b} 1658(m)^b	1552(w), 1528(w)	1972(s), 1675(m)^b	1560(w), 1535(w)
3	$[Rh_2(\eta^2\text{-HFB})_2(\mu\text{-CO})(\mu\text{-HFB})(dmpm)_2]$	1867(s)	1816(m), 1773(w), 1577(m)	1879(vs)^c 1840(s)^{c,d}	1816(s),^{c} 1773(m)^c 1583(m)^c
4	$[Rh(CO)(\mu\text{-HFB})(dmpm)]_2$	1971(s)	1559(m)	1981(w), 1978(s)^c 1933(s)^{c,d}	1559(w) 1560(w)^c
5	$[Rh_2(CO)_2(\eta^2\text{-HFB})(\mu\text{-HFB})(dmpm)_2]^e$			2077(s),^{c} 2033(s)^c	1776(w),^{c} 1590(w)^c

[a] Abbreviations used: vs, very strong; s, strong; m, medium; w, weak. [b] ν(CO) of CO_2Me . [c] THF solution. [d] ν(^{13}CO).

[e] Compound 5 was only observed in solution.

Table 5.2. NMR Spectroscopic Data for the Compounds in Chapter 5.[a,b]

	$\delta(^{31}P\{^1H\})^c$	$\delta(^{19}F)$	$\delta(^1H)$		
compound			P-CH$_3$	-CH$_2$-	-OCH$_3$
1	-4.66(d, 91.7 Hz)		1.59(s, 24H)	2.80(q, 4H, J= 5 Hz)	3.65(s, 6H)
2	-5.67(d, 91.1 Hz)	-54.7(s, 6F)	1.62(m, 12H), 1.56(m, 12H)	2.90(m, 2H), 2.61(m, 2H)	3.60(s, 6H)
3[d]	1.38(d, 98.0 Hz)	-52.27(s, 6F), -52.66(s, 6F), -53.88(s, 6F) -52.16(s, 6F),[e] -53.16(s, 6F),[e] -53.37(s, 6F)[e]	1.40(s, 12H), 1.29(s, 12H)	2.49(dq, 2H, J= 13.9, 5.5 Hz), 2.18(dq, 2H, J=13.8, 3.8 Hz)	
4	-6.46(d, 89.7 Hz)	-54.72(s, 12F)	1.60(m, 24H)	2.69(q, 4 H, J=5Hz)	
5	-11.4(m)	-47.08(qr, 3F, J= 15.9 Hz), -51.15(qr, 3F, J= 12.9 Hz), -53.64(qr, 3F, J= 12.9 Hz), -58.32(qr, 3F, J= 15.9 Hz)			

[a] Ambient temperature in CD_2Cl_2 except compound 3 and 5 (THF-d_8). [b] Abbreviations used: s, singlet; d, doublet; t, triplet; qr, quartet; q, quintet; dq, doublet of quintets; m, multiplet. [c] Vs 85% H_3PO_4, numbers in parentheses represent the separation in hertz between the two major peaks in the second-order spectrum of the complex. [d] $^{13}C\{^1H\}$ NMR of 3 (THF-d_8) at -40°C: δ 201.56 (t, $^1J_{C\text{-}Rh}$ 31.1 Hz). [e] -70°C.

After stirring for 10 min, the THF solvent was removed by cannula under positive N_2 pressure, the yellow solid was recrystallized from CH_2Cl_2/hexane and dried under vacuum. Compound **1** was obtained as a yellow powder in 38% yield (26 mg).

(b) [$Rh_2(CO)_2$(μ-DMAD)(μ-HFB)(dmpm)$_2$] (2). A purple solution of [$Rh_2(CO)_2$(μ-HFB)(dmpm)$_2$] (0.104 mmol based on 80% conversion of 100 mg, 0.130 mmol of [$Rh_2Cl_2(CO)_2$(μ-HFB)(dmpm)$_2$]) in THF (8 mL) was prepared as reported in Chapter 4. One equiv of DMAD (13 μL, 0.104 mmol) was added and the mixture stirred for 2 h. The solvent was removed under vacuum, the brown residue redissolved in a minimum volume of CH_2Cl_2 (ca. 6 mL) and the product precipitated with diethyl ether (20 mL). Upon cooling in an icebath, the solvent was removed by cannula under positive N_2 pressure and the solid was washed with diethyl ether. The orange-yellow product was dried under vacuum and isolated in 46% yield (50 mg). Anal. Calcd for $C_{22}F_6H_{34}O_6P_4Rh_2$: C, 31.5%; H, 4.1%. Found: C, 31.4%; H, 4.0%.

(c) [$Rh_2(\eta^2$-HFB)$_2$(μ-CO)(μ-HFB)(dmpm)$_2$] (3). A purple solution of [$Rh_2(CO)_2$(μ-HFB)(dmpm)$_2$] in THF (10 mL) was prepared as reported in Chapter 4 from [$Rh_2Cl_2(CO)_2$(μ-HFB)(dmpm)$_2$] (100 mg, 0.130 mmol). The dinitrogen atmosphere in the flask was replaced with an atmosphere of HFB and the solution was stirred for 1 h. The volume of the dark, brown-orange solution was reduced to ca. 5 mL under vacuum and the orange solid precipitated with hexane (25 mL). The solvents were removed by cannula under positive N_2 pressure, the solid washed with hexane and dried under vacuum. Compound **3** was isolated as an orange powder in

68% yield (95 mg). Anal. Calcd for $C_{27}F_{18}H_{36}O_2P_4Rh_2$: C, 30.5%; H, 3.4%. Found: C, 30.2%; H, 2.9%.

(d) [Rh(CO)(μ-HFB)(dmpm)]$_2$ (4). Compound 3 was prepared as described above using [$Rh_2Cl_2(CO)_2$(μ-HFB)(dmpm)$_2$] (100 mg, 0.130 mmol) and redissolved in THF (10 mL). The mixture was allowed to react under a static atmosphere of CO for 48 h. The static CO atmosphere was replenished twice over this time period. Within 24 h a yellow solid began to appear on the bottom of the flask. After two days the solvent was removed by evaporation under a stream of N_2 and the solid washed with two 10 mL aliquots of CH_2Cl_2. After drying the residue under a dinitrogen atmosphere, the product was isolated as a bright yellow solid in 46% yield (52 mg). The bright yellow solid was sparingly soluble in THF and CH_2Cl_2. Recrystallization of the product was effected from a THF/diethyl ether mixture. Anal. Calcd for $C_{20}F_{12}H_{28}O_2P_4Rh_2$: C, 28.0%; H, 3.3%. Found: C, 27.9%; H, 3.2%.

X-ray Data Collection. Yellow crystals of [$Rh_2(CO)_2$(μ-DMAD)(μ-HFB)(dmpm)$_2$] (**2**) were obtained by slow evaporation of an ethanol solution of [$Rh_2(CO)_2$(μ-DMAD)(dmpm)$_2$] which had been enriched with excess HFB. Yellow crystals of [Rh(CO)(μ-HFB)(dmpm)]$_2$ (**4**) were obtained by slow diffusion of diethyl ether into a concentrated THF solution. In both cases, suitable crystals did not appear to be air-sensitive and were thus mounted on glass fibers. Data were collected on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. Unit-cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections in the range $22.0° \leq 2\theta \leq 28.0°$ for compound **2** and $18.0° \leq 2\theta \leq 32.0°$ for compound **4**.

The diffraction symmetry and preliminary cell parameters for **2** suggested symmetry no higher than triclinic and the lack of systematic absences led to the choice of space group as $P1$ or $P\bar{1}$. A cell reduction [21] failed to detect a higher symmetry cell. Intensity d[illegible]ere collected at 22°C using the $\theta/2\theta$ scan technique to a maximum 2θ of 50.0°. For compound 4 the monoclinic diffraction symmetry and systematic absences (h0l, h+l= odd; 0k0, k= odd) were consistent with the space group $P\ 2_1/n$, a nonstandard setting of $P2_1/c$. Intensity data were collected as for **2** to a maximum 2θ of 56.0°. In both cases, backgrounds were obtained by increasing the scan 25% on each side of the peak. Three reflections were chosen as intensity standards, being remeasured at 120-min intervals of X-ray exposure. There was no significant variation in the intensities of these standards, and thus no decomposition correction was applied to either set of data. A total of 2711 reflections for compound **2** and 3687 reflections for compound **4** were measured and processed in the usual way, using a value of 0.04 for p [22] to downweight intense reflections. Of the reflections collected, 2486 were considered to be observed for **2** and 1588 were observed for **4** and were used in subsequent calculations. Absorption corrections were applied to the data using the method of Walker and Stuart.[21,23] See Tables 5.3 and 5.4 for a summary of crystal data and X-ray data collection information.

Structure Solution and Refinement. The structures of compounds **2** and **4** were solved in the space groups $P\bar{1}$ and $P2_1/n$, respectively. The heavy metal atoms were located by a Patterson map and all others by a

Table 5.3. Crystallographic Data for $[Rh_2(CO)_2(\mu\text{-DMAD})(\mu\text{-HFB})(dmpm)_2]$ (2).

compound	$[Rh_2(CO)_2(\mu\text{-DMAD})(\mu\text{-HFB})(dmpm)_2]$
formula weight	838.20
formula	$C_{22}F_6H_{34}O_6P_4Rh_2$
crystal shape	monoclinic prism
crystal dimensions, mm	0.109 × 0.253 × 0.447
space group	$P\bar{1}$ (No. 2)
temperature, °C	22
radiation (λ, Å)	graphite-monochromated Mo Kα (0.71069)
unit cell parameters	
a, Å	9.7825(8)
b, Å	9.832(1)
c, Å	9.3791(9)
α, deg	92.390(8)
β, deg	99.893(7)
γ, deg	118.180(8)
V, Å^3	775.53
Z	1
ρ(calcd), g cm^{-3}	1.795
linear absorption coeff (μ), cm^{-1}	13.196
range of transmission factors	0.914-1.060
detector aperture, mm	(3.00 + tan θ) wide × 4.00 high

Table 5.3. (continued)

takeoff angle, deg	3.0
maximum 2θ, deg	50.0
crystal-detector distance, mm	173
scan type	$\theta/2\theta$
scan rate, deg/min	between 1.67 and 6.67
scan width, deg	$0.80 + 0.347 \tan \theta$
total unique reflections	2711 ($h \pm k \pm l$)
total observations (NO)	2486
final no. parameters varied (NV)	235
error in obs. of unit wt. (GOF)[a]	1.922
R[a]	0.030
R_w[a]	0.049

[a] GOF, R and R_w are as defined in Table 2.3.

Table 5.4. Crystallographic Data for [Rh(CO)(μ-HFB)(dmpm)]$_2$ (4).

compound	[Rh(CO)(μ-HFB)(dmpm)]$_2$
formula weight	858.13
formula	$C_{20}F_{12}H_{28}O_2P_4Rh_2$
crystal shape	monoclinic prism
crystal dimensions, mm	0.090 × 0.106 × 0.115
space group	$P2_1/n$ (No. 14, nonstandard setting)
temperature, °C	22
radiation (λ, Å)	graphite-monochromated Mo Kα (0.71069)
unit cell parameters	
a, Å	9.474(1)
b, Å	15.812(2)
c, Å	9.917(1)
β, deg	95.33(1)
V, Å^3	1479.27
Z	2
ρ(calcd), g cm^{-3}	1.926
linear absorption coeff (μ), cm^{-1}	14.043
range of transmission factors	0.870-1.186
detector aperture, mm	(3.00 + tan θ) wide × 4.00 high
takeoff angle, deg	3.0

Table 5.4. (continued)

maximum 2θ, deg	50.0
crystal-detector distance, mm	173
scan type	$\theta/2\theta$
scan rate, deg/min	between 1.11 and 6.67
scan width, deg	$0.50 + 0.347 \tan \theta$
total unique reflections	3687 ($h\ k \pm l$)
total observations (NO)	1588
final no. parameters varied (NV)	181
error in obs. of unit wt. (GOF)[a]	1.067
R[a]	0.040
R_w[a]	0.043

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[a] GOF, R and R_w are as defined in Table 2.3.

sequence of full-matrix least-squares refinement and difference Fourier synthesis. All non-hydrogen atoms were ultimately located. Atomic scattering factors [24,25] and anomalous dispersion terms [26] were taken from the usual tabulations. All hydrogen atoms were included as fixed contributions but not refined. Their idealized positions were generated from the geometries about the attached carbon atoms, and they were assigned thermal parameters 20% greater than the equivalent isotropic B's of their attached carbon atoms.

For compound **2** ($Z = 1$) the structure was refined in both $P1$ and $P\bar{1}$. For the latter, the structure was disordered about the alkyne ligand atoms with the substituent atoms CF_3 and CO_2Me superimposed. Substantially lower R and R_w values were obtained for the centrosymmetric case ($P1$, $R = 0.064$, $R_w = 0.097$; $P\bar{1}$, $R = 0.030$, $R_w = 0.049$), and further support for the centrosymmetric space group was obtained by location of all hydrogens on dmpm and by satisfactory refinement of all atoms. The final model with 235 parameters refined,converged as shown in Table 5.3. In the final difference Fourier map, the 10 highest peaks (0.8-0.3 e/Å^3) were in the vicinity of the Rh, CF_3 and CO_2Me atoms. The positional parameters of all non-hydrogen atoms are listed in Table 5.5 and bond distances and angles are listed in Tables 5.6 and 5.7.

For the structure of compound **4** the final model with 181 refined, converged as shown in Table 5.4. In the final difference Fourier map, the 10 highest peaks (0.6 - 0.4 e/Å^3) were in the vicinity of the CF_3 atoms of HFB. The positional parameters of all non-hydrogen atoms are listed in Table 5.8 and bond distances and angles are listed in Tables 5.9 and 5.10.

Table 5.5. **Positional and Thermal Parameters for $[Rh_2(CO)_2(\mu\text{-DMAD})(\mu\text{-HFB})(dmpm)_2]$ (2).[a]**

Atom	x	y	z	*B*(Å^2)
Rh	-0.04955(2)	-0.15392(2)	-0.00502(2)	2.256(5)
P(1)	-0.2058(1)	-0.1839(1)	0.1624(1)	3.33(2)
P(2)	-0.0941(1)	0.1532(1)	0.1771(1)	3.35(2)
F(1)	-0.3914(8)	-0.3900(7)	-0.2536(7)	9.5(2)
F(2)	-0.3304(9)	-0.2400(9)	-0.4106(6)	9.4(3)
F(3)	-0.4842(5)	-0.2544(6)	-0.2784(9)	8.2(2)
F(4)	-0.3901(6)	0.0368(7)	-0.272(1)	9.9(2)
F(5)	-0.2432(8)	0.0614(7)	-0.4111(7)	9.0(2)
F(6)	-0.1697(6)	0.2485(5)	-0.2380(7)	8.2(2)
O(1)	-0.1715(4)	-0.5008(4)	-0.0236(5)	7.8(1)
O(2)	0.3292(7)	-0.1272(7)	0.2489(8)	9.4(2)
O(3)	0.1662(8)	-0.1233(8)	0.3918(6)	6.4(2)
O(4)	0.3634(9)	0.3807(8)	0.279(1)	12.6(3)
O(5)	0.4273(8)	0.1964(8)	0.3554(9)	10.9(2)
C(1)	-0.1237(4)	-0.3695(4)	-0.0144(5)	4.2(1)
C(2)	-0.3449(4)	-0.2465(4)	-0.2754(4)	3.93(9)
C(3)	-0.2065(4)	-0.1215(4)	-0.1703(4)	2.82(7)
C(4)	-0.1577(3)	0.0301(4)	-0.1671(4)	2.69(7)
C(5)	-0.2269(5)	0.0991(5)	-0.2721(5)	5.7(1)
C(6)	0.337(1)	-0.234(1)	0.383(1)	9.0(3)
C(7)	0.560(1)	0.312(1)	0.475(1)	7.6(3)

Table 5.5. (continued).

C(8)	-0.1405(4)	-0.0076(5)	0.2838(4)	4.19(9)
C(9)	-0.2123(6)	-0.3211(5)	0.2881(5)	5.9(1)
C(10)	-0.4162(5)	-0.2551(6)	0.0885(6)	5.8(1)
C(11)	-0.2821(4)	0.1482(5)	0.1117(5)	5.3(1)
C(12)	0.0051(6)	0.3244(6)	0.3176(5)	6.1(1)

[a] All atoms are refined anisotropically as defined in Table 2.4, Chapter 2.

Table 5.6. Bond Distances (Å) for [$Rh_2(CO)_2$(μ-DMAD)(μ-HFB)$(dmpm)_2$] (2).

Rh-Rh'	2.6989(4)	F(3)-C(2)	1.323(6)
Rh-P(1)	2.3080(8)	F(4)-C(5)	1.41(1)
Rh-P(2)'	2.3132(8)	F(5)-C(5)	1.30(1)
Rh-C(1)	1.881(3)	F(6)-C(5)	1.302(7)
Rh-C(3)	2.133(3)	O(1)-C(1)	1.140(4)
Rh'-C(4)	2.140(3)	O(2)-C(5)'	1.21(1)
P(1)-C(8)	1.803(4)	O(2)-C(6)	1.68(1)
P(1)-C(9)	1.814(4)	O(3)-C(5)'	1.34(1)
P(1)-C(10)	1.820(4)	O(4)-C(2)'	1.24(1)
P(2)-C(8)	1.821(4)	O(5)-C(2)'	1.286(8)
P(2)-C(11)	1.813(4)	O(5)-C(7)	1.50(1)
P(2)-C(12)	1.829(4)	C(2)-C(3)	1.478(4)
F(1)-C(2)	1.300(9)	C(3)-C(4)	1.331(4)
F(2)-C(2)	1.301(6)	C(4)-C(5)	1.465(4)

Table 5.7. Bond Angles (deg) for $[Rh_2(CO)_2(\mu\text{-DMAD})(\mu\text{-HFB})(dmpm)_2]$ (2).

Rh'-Rh-P(1)	93.13(2)	C(11)-P(2)-C(12)	100.9(2)
Rh'-Rh-C(1)	178.6(1)	C(5)'-O(2)-C(6)	101.2(9)
Rh'-Rh-C(3)	71.17(7)	C(2)'-O(5)-C(7)	116.8(7)
P(1)-Rh-P(2)'	173.75(3)	Rh-C(1)-O(1)	178.1(4)
P(1)-Rh-C(1)	86.4(1)	F(1)-C(2)-F(2)	106.7(7)
P(1)-Rh-C(3)	92.30(7)	F(1)-C(2)-F(3)	95.3(7)
P(1)-Rh-C(4)'	89.38(7)	F(1)-C(2)-C(3)	118.2(5)
C(1)-Rh-C(3)	107.6(1)	F(2)-C(2)-F(3)	104.0(6)
Rh-Rh'-P(2)	93.03(2)	F(2)-C(2)-C(3)	113.6(4)
Rh-Rh'-C(4)	71.46(7)	F(3)-C(2)-C(3)	116.9(4)
P(2)-Rh'-C(3)'	88.70(7)	O(4)-C(2)'-O(5)	129.1(8)
P(2)-Rh'-C(4)	93.56(7)	O(4)-C(2)'-C(3)'	117.8(7)
C(1)'-Rh'-C(4)	109.8(1)	O(5)-C(2)'-C(3)'	113.1(4)
Rh-P(1)-C(8)	113.6(1)	Rh'-C(3)'-C(2)'	125.8(2)
Rh-P(1)-C(9)	115.3(1)	Rh-C(3)-C(4)	109.3(2)
Rh-P(1)-C(10)	116.6(1)	C(2)-C(3)-C(4)	125.0(3)
C(8)-P(1)-C(9)	102.6(2)	Rh'-C(4)-C(3)	108.1(2)
C(8)-P(1)-C(10)	105.3(2)	Rh'-C(4)-C(5)	126.4(2)
C(9)-P(1)-C(10)	101.7(2)	C(3)-C(4)-C(5)	125.3(3)
Rh'-P(2)-C(8)	113.6(1)	F(4)-C(5)-F(5)	97.3(7)
Rh'-P(2)-C(11)	117.3(1)	F(4)-C(5)-F(6)	103.4(6)
Rh'-P(2)-C(12)	115.3(1)	F(4)-C(5)-C(4)	109.3(5)
C(8)-P(2)-C(11)	105.0(2)	F(5)-C(5)-F(6)	111.6(6)
C(8)-P(2)-C(12)	102.9(2)	F(5)-C(5)-C(4)	118.7(6)

Table 5.7. (continued).

F(6)-C(5)-C(4)	114.0(3)	O(3)-C(5)'-C(4)'	112.9(6)
O(2)-C(5)'-O(3)	125.7(8)	P(1)-C(8)-P(2)	108.8(2)
O(2)-C(5)'-C(4)'	121.3(6)		

Table 5.8. **Positional and Thermal Parameters for $[\mathrm{Rh(CO)(\mu\text{-}HFB)(dmpm)}]_2$ (4).**[a]

Atom	x	y	z	B(Å^2)
Rh	0.01230(6)	0.05184(4)	0.10839(6)	2.110(9)
P(1)	0.1661(2)	-0.0388(1)	0.2336(2)	2.83(4)
P(2)	0.1437(2)	-0.1513(1)	-0.0072(2)	3.11(5)
F(1)	-0.2732(7)	-0.0999(4)	0.3019(6)	9.1(2)
F(2)	-0.3914(6)	-0.0066(5)	0.1952(6)	9.3(2)
F(3)	-0.2230(6)	0.0270(4)	0.3332(5)	7.3(2)
F(4)	0.4111(6)	0.1168(5)	0.039(1)	13.3(3)
F(5)	0.2975(8)	0.2033(4)	-0.0791(7)	13.9(2)
F(6)	0.2720(7)	0.1924(4)	0.1177(7)	9.5(2)
O(1)	0.0483(7)	0.1725(4)	0.3466(6)	6.1(2)
C(1)	0.0332(8)	0.1264(5)	0.2573(8)	3.4(2)
C(2)	-0.2597(9)	-0.0290(6)	0.2360(9)	4.4(2)
C(3)	-0.1641(7)	-0.0307(4)	0.1257(8)	2.6(2)
C(4)	0.1770(7)	0.0810(5)	-0.0178(8)	2.5(2)
C(5)	0.2855(9)	0.1470(6)	0.0117(9)	4.5(2)
C(6)	0.088(1)	-0.1064(6)	0.3554(9)	4.9(2)
C(7)	0.3082(9)	0.0115(6)	0.3409(9)	4.5(2)
C(8)	0.2632(8)	-0.1099(5)	0.1311(8)	3.2(2)
C(9)	0.265(1)	-0.1986(6)	-0.117(1)	4.8(2)
C(10)	0.065(1)	-0.2448(6)	0.061(1)	5.6(3)

[a] All atoms are refined anisotropically as defined in Table 2.4, Chapter 2.

Table 5.9. Bond Distances (Å) for [Rh(CO)[illegible]HFB)(dmpm)]$_2$ (4).

Rh-Rh'	2.696(1)	P(2)-C(10)	1.82(1)
Rh-P(1)	2.320(2)	F(1)-C(2)	1.31(1)
Rh'-P(2)	2.322(2)	F(2)-C(2)	1.32(1)
Rh-C(1)	1.886(9)	F(3)-C(2)	1.33(1)
Rh-C(3)	2.140(7)	F(4)-C(5)	1.29(1)
Rh-C(4)	2.139(8)	F(5)-C(5)	1.28(1)
P(1)-C(6)	1.821(9)	F(6)-C(5)	1.30(1)
P(1)-C(7)	1.820(9)	O(1)-C(1)	1.146(9)
P(1)-C(8)	1.821(8)	C(2)-C(3)	1.48(1)
P(2)-C(8)	1.818(8)	C(3)-C(4)	1.33(1)
P(2)-C(9)	1.816(9)	C(4)-C(5)	1.47(1)

Table 5.10. Bond Angles (deg) for [Rh(CO)(μ-HFB)(dmpm)]$_2$ (4).

Rh'-Rh-P(1)	93.13(6)	C(8)-P(2)-C(9)	102.5(4)
Rh'-Rh-C(1)	178.4(3)	C(8)-P(2)-C(10)	105.1(4)
Rh'-Rh-C(3)	71.5(2)	C(9)-P(2)-C(10)	101.2(5)
Rh'-Rh-C(4)	71.2(2)	Rh-C(1)-O(1)	178.6(8)
Rh-Rh'-P(2)	93.61(6)	F(1)-C(2)-F(2)	104.5(8)
P(1)-Rh-P(2)'	173.11(8)	F(1)-C(2)-F(3)	103.8(8)
P(1)-Rh-C(1)	87.2(2)	F(1)-C(2)-C(3)	116.6(8)
P(1)-Rh-C(3)	92.1(2)	F(2)-C(2)-F(3)	102.6(8)
P(1)-Rh-C(4)	89.4(2)	F(2)-C(2)-C(3)	113.7(8)
P(2)'-Rh-C(1)	86.1(2)	F(3)-C(2)-C(3)	114.2(8)
P(2)'-Rh-C(3)	88.7(2)	Rh-C(3)-C(2)	125.7(6)
P(2)'-Rh-C(4)	94.1(2)	Rh-C(3)-C(4)'	108.4(5)
C(1)-Rh-C(3)	110.1(3)	C(2)-C(3)-C(4)'	126.0(7)
C(1)-Rh-C(4)	107.1(3)	Rh-C(4)-C(3)'	108.9(5)
C(3)-Rh-C(4)	142.7(3)	Rh-C(4)-C(5)	124.8(6)
Rh-P(1)-C(6)	116.3(3)	C(3)'-C(4)-C(5)	126.4(8)
Rh-P(1)-C(7)	115.9(3)	F(4)-C(5)-F(5)	105(1)
Rh-P(1)-C(8)	114.0(3)	F(4)-C(5)-F(6)	101.3(9)
C(6)-P(1)-C(7)	101.1(5)	F(4)-C(5)-C(4)	113.2(9)
C(6)-P(1)-C(8)	105.4(4)	F(5)-C(5)-F(6)	102(1)
C(7)-P(1)-C(8)	102.3(4)	F(5)-C(5)-C(4)	117.4(8)
Rh'-P(2)-C(8)	114.1(3)	F(6)-C(5)-C(4)	115.8(8)
Rh'-P(2)-C(9)	115.7(3)	P(1)-C(8)-P(2)	109.4(4)
Rh'-P(2)-C(10)	116.5(3)		

Results and Discussion

(a) Description of Structures. Perspective views of compounds $[Rh_2(CO)_2(\mu\text{-DMAD})(\mu\text{-HFB})(dmpm)_2]$ (**2**) and $[Rh(CO)(\mu\text{-HFB})(dmpm)]_2$ (**4**) indicating the labeling schemes are presented in Figures 5.1 and 5.2. In both cases the asymmetric unit represents one half of the molecule with the other half being related by an inversion centre situated midway between the two metals. As suggested by the spectroscopic data (Tables 5.1 and 5.2) and as shown in Figures 5.1 and 5.2, both structures are symmetric. In each, the metal centres are held together by the two bridging diphosphine ligands and two alkyne ligands. The dmpm ligands have the classical trans arrangement found in many dppm-bridged [12-15,27,28] and dmpm-bridged binuclear species [29-32] (see also Chapter 2). The two alkyne ligands occupy equatorial positions on opposite faces of the "$Rh_2(dmpm)_2$" core. Both are coordinated in a cis-dimetalated fashion with the two rhodium atoms and all four unsaturated carbon atoms of the alkynes essentially in the same plane (torsion angles between the atoms C3-Rh-Rh'-C3'= 180.0(4)° for both structures). Each metal has a terminal carbonyl attached to it which is also in the equatorial plane and along the metal-metal axis. In both complexes the rhodium atoms are regarded as Rh(II) centers, viewing the bridging alkyne ligands as dianionic. If the single metal-metal bond is taken into account, each metal atom has a coordination number of six with a geometry resembling that of a distorted octahedron.

The diphosphine groups bridge the two Rh(II) centres in a typical trans arrangement (P(1)-Rh-P(2)'= 173.75(3)° for compound **2**;

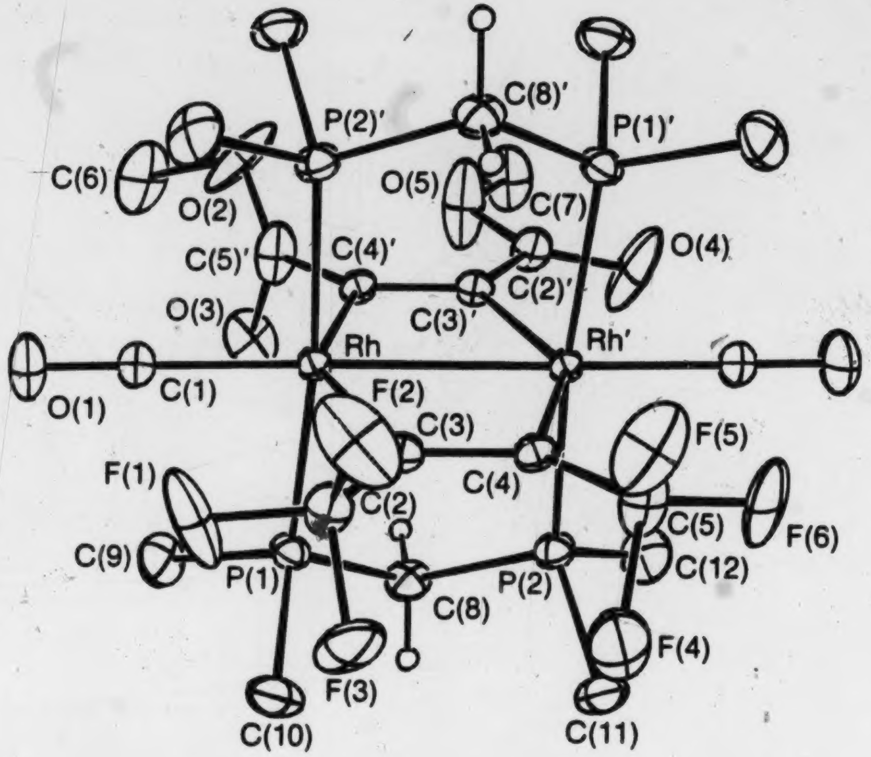


Figure 5.1. A perspective view of $[Rh_2(CO)_2(\mu\text{-DMAD})(\mu\text{-HFB})(dmpm)_2]$ (2) showing the numbering scheme. Thermal parameters are shown at the 20% level except for methylene hydrogens which are drawn artifically small. Hydrogen atoms on the methyl groups are omitted for the sake of clarity.

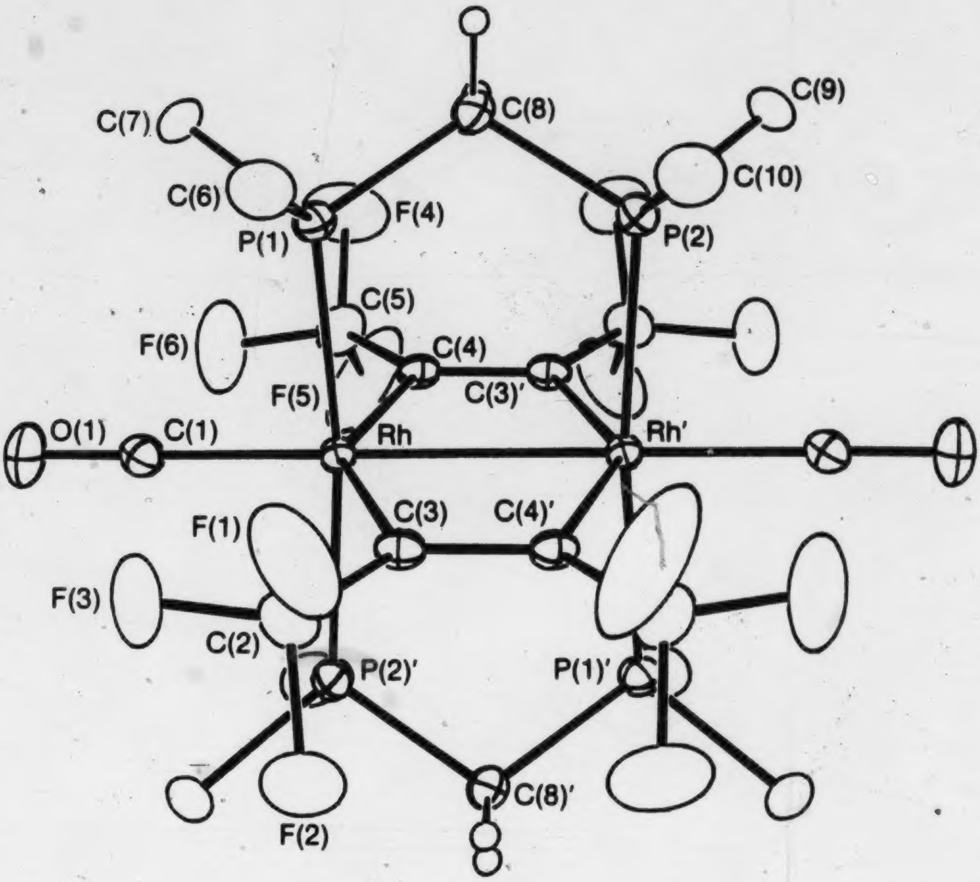


Figure 5.2. A perspective view of $[Rh(CO)(\mu\text{-}HFB)(dmpm)]_2$ (4) showing the numbering scheme. Thermal parameters are shown at the 20% level except for methylene hydrogens which are drawn artifically small. Hydrogen atoms on the methyl groups are omitted for the sake of clarity.

P(1)-Rh-P(2)'= 173.11(8)° for compound 4) and are eclipsed with regards to each other about the Rh-Rh bond with a torsion angle (P(1)-Rh-Rh'-P(2)) of 1.04(4)° for **2** and 1.42(8)° for **4**. The Rh-P distances (2.3080(8)-2.3132(8) Å for **2** and 2.320(2) - 2.322(2) for **4**) are similar to values in related Rh(II) complexes bridged by dmpm (Chapter 2) and dppm [12c,12f,13c] (range 2.301(2) - 2.384(2) Å).

In both compounds distortion from octahedral geometry results from the restrictions imposed by the two bridging alkyne groups. Therefore, C_{alkyne}-Rh-Rh' angles (ca. 71.46(7)° and 71.2(2)°, see Tables 5.7 and 5.10) and C_{alkyne}-Rh-CO angles (ca. 107.6(1)-109.8(1)° and 107.1(3)-110.1(3)°, see Tables 5.7 and 5.10) are significantly different from 90°. These acute angles are representative of those found in other metal-metal bonded complexes which are bridged by a single cis-dimetalated olefin.[12c,12e,12f,33,34] Alternatively, the geometry could be discussed as trigonal bipyramidal by ignoring the Rh-Rh' bond.

Although the Rh-Rh' separation of 2.6989(4) Å in **2** and 2.696(1) Å in **4** falls within the range of normal Rh-Rh single bonds in related diphosphine systems (2.682(1)-2.9653(6) Å),[12c,12e,12f,33,35,36] they are clearly on the short end of the range observed in other binuclear Rh(II) compounds in which the Rh atoms are bridged by cis-dimetalated olefins.[12c,12f,13c,33] Compression along the Rh-Rh' axis, through mutual attraction of the metals, is apparent upon comparison of the Rh-Rh' distances with the intraligand P···P separation (nonbonded intraligand P-P separation = 2.947(1) Å for **2**; 2.969(3) Å for **4**).

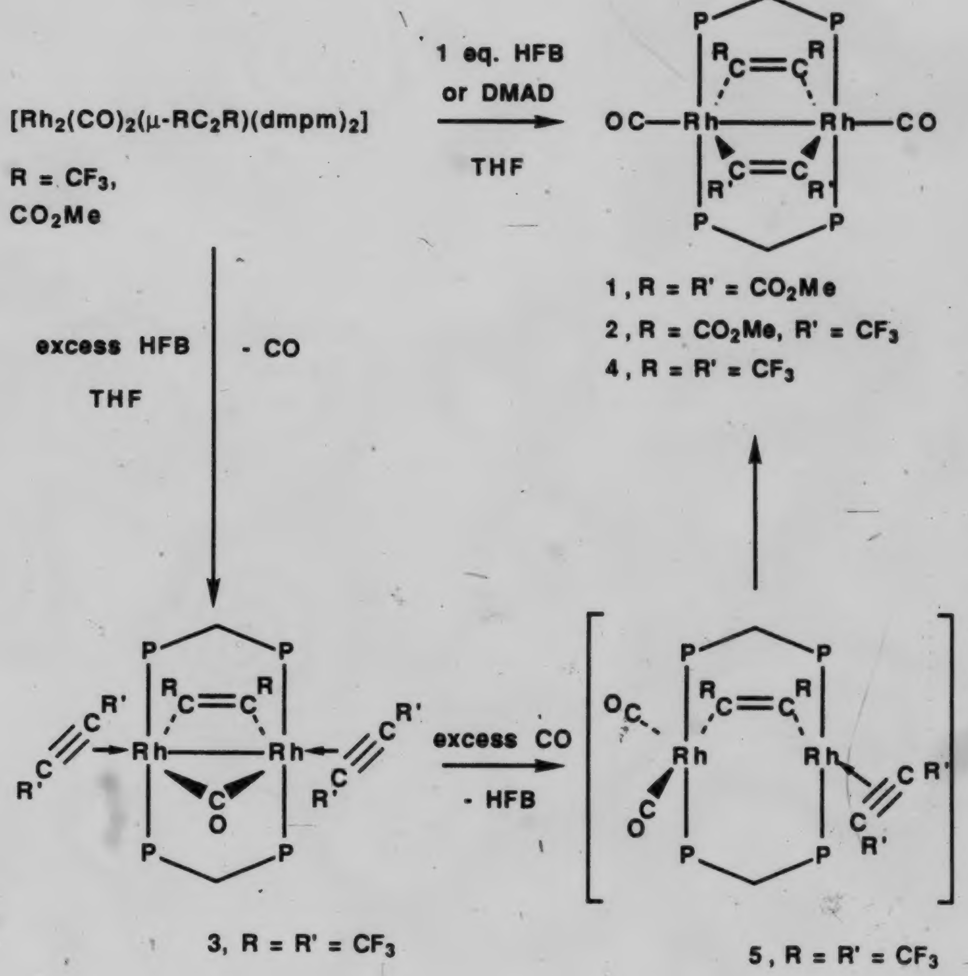
The Rh-C_{alkyne} distances (2.133(3)-2.140(3) Å for **2**; 2.139(8)-2.140(7) Å for 4) are noticeably longer than those in "Rh_2(diphosphine)$_2$" compounds containing only one bridged alkyne unit (range 1.994(9)-2.089(4) Å).[12c,12f,13c,33] Presumably this is a reflection of the strain imposed on the unsaturated carbon atoms by the relatively short Rh-Rh' distances of compounds **2** and **4**. Indeed, distortion from the idealized sp^2 hybridization of these carbon atoms is evident in the compressed Rh-C_{alkyne}-C_{alkyne} angles (Rh-C(3)-C(4)= 109.3(2)° for **2** and Rh-C(3)-C(4)'= 108.4(5)° for **4**). Apart from the Rh-C_{alkyne} separation, the bond distances about the unsaturated carbon atoms of each alkyne ligand correspond to those of the "M_2(μ-alkyne)" unit in monoalkyne, metal-metal bonded complexes.[12c,12f,13c,19,33,34] The C_{alkyne}-C_{alkyne} -R angles (C(2)-C(3)-C(4)= 125.0(3)°, C(3)-C(4)-C(5)= 125.3(3)° for **2**; C(2)-C(3)-C(4)'=126.0(7)°, C(3)'-C(4)-C(5)= 126.4(8)° for **4**) are similar to the appropriate values in the above monoalkyne species. The C(3)-C(4) and C(3)-C(4)' distances within the acetylenic unit (1.331(4) Å for **2**; C-C= 1.33(1) Å for **4**) are close to those of olefinic double bonds,[37] and are the same as values observed for "M_2(μ-alkyne)" systems with and without metal-metal bonds.[12,13b,13c,19,28,29,34]

Due to the inversion centre situated midway between the metal atoms, the substituents on the alkyne α-carbon of compound **2** are disordered with respect to each other so the CO_2Me and CF_3 groups are superimposed on electron density maps. Despite this disorder, the substituents are rather well defined and have their expected geometries. Furthermore it is clear that the two carboxylate groups of DMAD are perpendicular to each other (interplaner angle 97.4(1)°) with one in the equatorial plane of the molecule and the other out of the plane (Figure 5.1). This represents the typical arrangement observed in related binuclear complexes bridged by a DMAD group,[12d,12e,12g,13b,13d,38,39] and is one which clearly minimizes the contact between substituent groups and the diphosphine substituents.

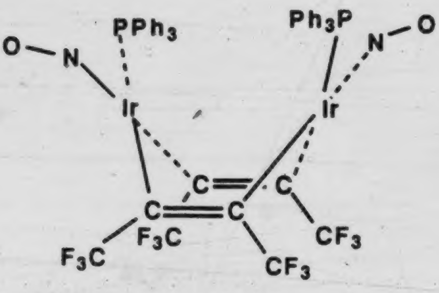
(b) Description of Chemistry. The bis(alkyne) complexes $[Rh(CO)(\mu\text{-DMAD})(dmpm)]_2$ (**1**) and $[Rh_2(CO)_2(\mu\text{-DMAD})(\mu\text{-HFB})(dmpm)_2]$ (**2**) are prepared via the addition of one equiv of DMAD to a solution of $[Rh_2(CO)_2(\mu\text{-DMAD})(dmpm)_2]$ or $[Rh_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$, respectively. The preparation of complex **1** can also be achieved from the addition of two equiv of DMAD to $[Rh_2(CO)_3(dmpm)_2]$, but the former method represents the more convenient route. The third member in this series, $[Rh(CO)(\mu\text{-HFB})(dmpm)]_2$ (**4**), is obtained upon long term reaction of CO with the complex $[Rh_2(\eta^2\text{-HFB})_2(\mu\text{-CO})(\mu\text{-HFB})(dmpm)_2]$ (**3**), which is in turn prepared from the reaction of excess HFB with $[Rh_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ (vide infra). These reactions are summarized in Scheme 5.1. All species are coordinatively-saturated 18 electron complexes which exhibit a much greater degree of air-stability than their precursors. No subsequent reaction of the three bis(alkyne) complexes with excess CO, DMAD, HFB or $HBF_4{\bullet}OEt_2$ was found to take place.

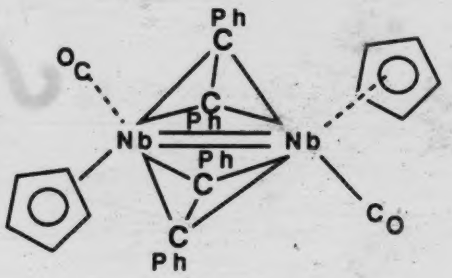
Binuclear diphosphine-bridged compounds containing a bridging alkyne molecule are quite common,[12-17,38,39] but compounds **1**, **2** and **4** are the first such species in which two alkyne ligands have been successfully coordinated at the metal centres as cis-dimetalated olefins. They also represent the first examples of binuclear bis(alkyne) complexes in which

Scheme 5.1


$[Rh_2(CO)_2(\mu\text{-}RC_2R)(dmpm)_2]$
R = CF_3,
CO_2Me
1 eq. HFB
or DMAD
THF
1, R = R' = CO_2Me
2, R = CO_2Me, R' = CF_3
4, R = R' = CF_3
excess HFB
THF
- CO
excess CO
- HFB
3, R = R' = CF_3
5, R = R' = CF_3

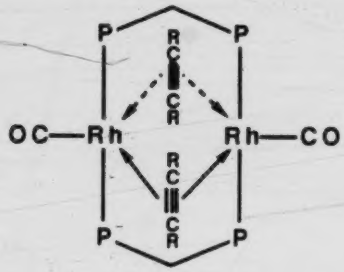
the two metal atoms and the two unsaturated carbon atoms of each alkyne unit lie in a single plane. Other examples of bimetallic bis(alkyne) species [40-47] form either a boat conformation without a metal-metal bond as in $[Ir(\mu\text{-HFB})(NO)(PPh_3)]_2$,[40] or have perpendicularly-coordinated alkyne ligands with a metal-metal bond as in $[CpNb(CO)(\mu\text{-}PhC_2Ph)]_2$.[43] In contrast to complexes **1**, **2** and **4**, these other binuclear bis(alkyne) species have been prepared via the reaction of a mononuclear starting material with a specific alkyne molecule. The only exception to this is $[Fe(CO)_2\{\mu\text{-}\eta^2\text{-}(^t\text{Bu-CC-}^t\text{Bu})\}]_2$, which is obtained from the reaction of $Fe_3(CO)_{12}$ with di-*t*-butylacetylene.[44] It has been suggested that the reaction of these mononuclear species proceeds via the dimerization of a 1, 3-dipolar intermediate, $[L_xM^+(RC{=}CR^-)]$.[42] For the dimeric cases presented here, we have no evidence to suggest a mechanism which involves dipolar intermediates in these reactions.





It seems apparent that the low oxidation state of the metals and the basic nature of the dmpm ligands are important factors in the coordination of a second electrophilic alkyne ligand. Not surprisingly, the unactivated alkynes diphenylacetylene and 2-butyne (which are better electron donors but poorer π–acceptors than either of DMAD and HFB) are unreactive towards the starting materials [$Rh_2(CO)_2$(μ-alkyne)$(dmpm)_2$] (alkyne= DMAD, HFB). In addition, the reduced steric bulk of the dmpm ligand is also a factor in the reactivity, allowing the second alkyne ligand room to coordinate with a minimum of steric interference from the diphosphine substituents. By comparison, we note that the related species [$Ir_2(CO)_2$(μ-η^2-DMAD)$(dppm)_2$] which contains the more bulky dppm ligands does not react with a second equiv of DMAD.[12g]

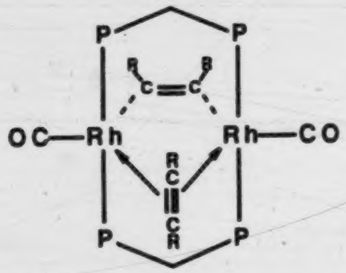
The planarity of the "$Rh_2(alkyne)_2$" fragment in these complexes can be rationalized from both steric and electronic arguments. Using the convention that perpendicularly-coordinated alkyne ligands are neutral, 4-electron donors and that parallel alkyne ligands are dianionic 4-electron donors, we see that the former type of coordination would provide an unfavourable 19 electron species, **A**. From a steric point of view, the alkyne ligands in **A** would have an unfavourable interaction with the



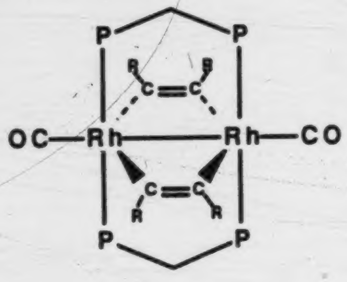
A

diphosphine ligands, since, with alkyne molecules coordinated on both sides of the Rh_2P_4 framework, the diphosphine ligands cannot bend away from either alkyne ligand into a cis-cis geometry as in the monoalkyne complexes $[Rh_2(CO)_2(\mu\text{-}\eta^2\text{-}PhC_2Ph)(dppm)_2]$ [16b] and $[Ir_2(CO)_2(\mu\text{-}\eta^2\text{-}DMAD)(dppm)_2]$.[12g]

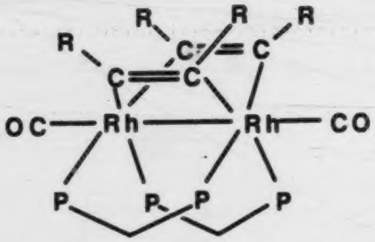
Other possible forms of alkyne coordination are shown in **B**, **C**, and **D**. Structure **B**, with one perpendicular and one parallel coordinated alkyne ligand is an 18 electron species but large, unfavourable steric interactions between the diphosphine ligands and at least one alkyne would be expected. The third possibility, **C** (also an 18 electron species), with both alkyne ligands coordinated parallel to the metal-metal vector is anticipated to have the least steric hindrance. It has the added advantage of



B



C



D

a metal-metal bond and therefore would be expected to be thermodynamically favoured over **B**.

It is interesting to note that structure D has not yet been observed. This structure would have an alignment of the alkyne ligands which is analogous to that of the diiridium species[40] shown earlier. The mutally cis, cis-diphosphine arrangement has been observed in several previous binuclear cases with the more bulky phenyl substituents of dppm,[12g,16b,48,49] however, these dppm complexes have only one other bridging ligand. For complexes **1, 2** and **4**, it may be that the incorporation of two bridging-alkyne ligands would create unfavourable steric interactions between themselves and the dmpm ligands, even when the diphosphine substituents are the relatively small Me groups. It is assumed that the actual structure of complexes **1, 2**, and **4**, with the alkyne ligands on opposite faces of the dimer, is a consequence of the availability of a site of alkyne attack.

The spectroscopic characterization of the bis(alkyne) compounds **1, 2** and **4** is straightforward (see Tables 5.1 and 5.2). Each exhibits a second order resonance in the $^{31}P\{^1H\}$ NMR comprised of two principal peaks, which is consistent with the spin system AA'A''A'''XX'. The pattern is typical of those observed for symmetrical "$Rh_2(dmpm)_2$"[31,32] (see also Chapter 2) and "$Rh_2(dppm)_2$"[27,28] complexes. The methyl protons (ca. δ 1.6) and methylene protons (ca. δ 2.8) of the dmpm ligands appear in the ^1H NMR spectra as either one or two resonances depending on whether each side of the plane defined by the Rh_2P_4 framework of the complex is the same as in **1** and **4** (one resonance) or different as in **2** (two resonances). The methyl protons belonging to the carboxylate group in **1** and **2** are present as additional resonances at ca. δ 3.60 (singlets). Complexes **2** and **4** exhibit a single resonance each for the requisite fluorine atoms of coordinated hexafluoro-2-butyne at ca. δ -55.0 in the ^{19}F NMR spectra.

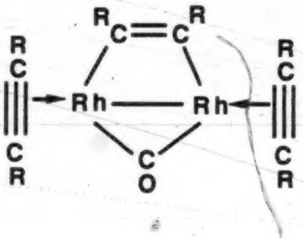
A single terminal CO stretch is observed in the infrared spectra for each of **1**, **2** and **4**, and a general increase in frequency of this band (ca. 9 cm^{-1} in THF solution) is noted as each DMAD ligand is replaced by HFB. This trend reflects the greater group electronegativity of the CF_3 group relative to CO_2Me,[50] and the greater electron withdrawing ability of HFB over DMAD. The ensuing reduction in the amount of π-backbonding from the metal into the π^* orbitals of CO produces a higher frequency CO stretch for the HFB complexes. Additional carbonyl bands of note in the infrared region include those due to the carboxylate moiety of **1** and **2**, ranging form 1675 cm^{-1} to 1650 cm^{-1}. Weak bands appearing in the vicinity of 1525 cm^{-1} to 1560 cm^{-1} have been assigned to the unsaturated carbon-carbon stretching vibrations of the alkyne ligands.

The addition of excess HFB to $[Rh_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ was originally investigated as a means of preparing the bis(alkyne) complex **4** and in an attempt to induce the coupling of alkyne molecules. Neither of these objectives were initially achieved.The reaction instead involves the coordination of two additional alkyne units and loss of CO from the starting material to yield the unusual species $[Rh_2(\eta^2\text{-HFB})_2(\mu\text{-CO})(\mu\text{-HFB})\text{-}(dmpm)_2]$ (**3**) which contains three alkyne groups (see Scheme 5.1). The preparation of complex **3** represents one of only a few examples of a binuclear diphosphine complexes in which an alkyne molecule is terminally bonded to one metal centre in a η^2 fashion[18] and appears to be the only one in which three indepentent alkyne ligands are incorporated into a binuclear complex. The reaction appears to be quantitative, and we see no spectroscopic evidence to suggest the presence of HFB insertion or polymeric HFB products.

Each of the two new HFB molecules in compound **3** is coordinated to a single metal atom as terminal, π-bound alkyne ligands and are formally counted as neutral 2-electron donor ligands. In the infrared spectrum two C=C stretches for the terminally coordinated alkyne ligands appear at 1816 cm^{-1} and 1773 cm^{-1} , approximately midway between that observed for free HFB (ν(CC)= 2300 cm^{-1}, Raman) [51] and that of cis-dimetalated HFB (ν(CC)= 1583 cm^{-1} for **3**). Similar values have been found for the η^2-coordinated HFB ligand in the dinuclear species $[Ir_2(CO)(\eta^2\text{-HFB})(\mu\text{-S})(\mu\text{-CO})(dppm)_2]$ (ν(CC)= 1747 cm^{-1})[18] and $[Ir_2(CO)_2(\eta^2\text{-HFB})(P(O\text{-}t\text{-Bu})_3)_2(\mu\text{-S-}t\text{-Bu})_2]$ (ν(CC)= 1765 cm^{-1}).[52] The higher frequency C-C stretches indicate that the carbon-carbon bond of the newly coordinated η^2-HFB moieties retain more multiple bond character and therefore have a much weaker interaction with the Rh centres than cis-dimetalated HFB. In accordance with this hypothesis, compound **3** is found to undergo loss of one η^2-HFB ligand and migration of the second η^2-HFB into a cis-dimetalated position, yielding the bis(alkyne) complex **4** upon reaction with CO. It is clear that the trialkyne species $[Rh_2(\eta^2\text{-HFB})_2\text{-}(\mu\text{-CO})(\mu\text{-HFB})(dmpm)_2]$ (**3**) is not formed from the dibridged species $[Rh(CO)(\mu\text{-HFB})(dmpm)]_2$ (**4**) since the reaction is not reversible. These results are consistent with the inability of the bis(alkyne) species **1**, **2** and **4** to react with CO once both alkyne ligands become coordinated as cis-dimetalated olefins.

Other prominent infrared vibrations of compound **3** include the bridging CO stretch at 1879 cm^{-1} (THF). An isotopic shift of this band to 1840 cm^{-1} in the infrared spectrum of a ^{13}CO enriched sample of **3** confirms the assignment. The same sample produces a single resonance in the CO region of the $^{13}C\{^1H\}$ NMR spectrum at δ 201.56 (triplet). The chemical shift and one bond C-Rh coupling value of 31.1 Hz is typical of those observed for other CO-bridged dirhodium complexes (see Chapter 4, Table 4.2).

The presence of three resonances, all of equal intensity, in the ^{19}F NMR spectrum of **3** implies a lack of rotation of the two new HFB ligands about the alkyne-metal vector and defines the orientation of the two η^2-HFB ligands as perpendicular to the P-Rh-P vector. Thus each CF_3 group on the two terminally bound HFB ligands remains in a distinct environment, one being on the same side of the complex as the bridging CO and the other on the same side as the cis-dimetalated olefin, giving rise to a total of two resonances. The fact that these two resonances appear as broad singlets and not resolved quartets (even at low temperature, -70°C)

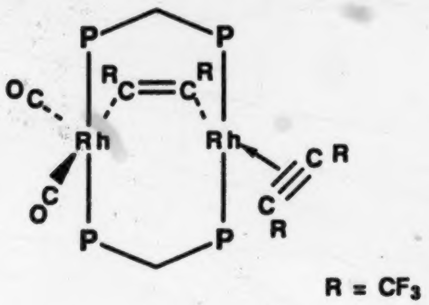


R = CF_3

implies that the intraligand F-F coupling is too small to be resolved. The third resonance is assigned to the two CF_3 groups on the cis-dimetallated HFB ligand. These data are consistent with the hypothesis that the two η^2-HFB ligands would adopt a configuration which is perpendicular to the "Rh_2P_4" plane in order to minimize contact with the dmpm ligands.

As mentioned previously, $[Rh_2(\eta^2\text{-HFB})_2(\mu\text{-CO})(\mu\text{-HFB})(dmpm)_2]$ (3) loses one equivalent of HFB slowly under a CO atmosphere yielding the bis(alkyne) product **4**. There is no spectroscopic evidence to suggest the loss of two HFB ligands from compound **3** to yield the original starting material, $[Rh_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$, during the reaction. The mild conditions under which HFB is lost is reminiscent of the behaviour exhibited by the related species $[Ir_2(CO)_2(\eta^2\text{-HFB})(\mu\text{-S})(\mu\text{-CO})(dppm)_2]$ which loses HFB upon reflux in CH_2Cl_2.[18] This lability appears to be restricted to η^2-alkynes since the removal of cis-dimetalated olefin ligands in general has not been observed for binuclear diphosphine complexes.[12f,20] In fact, the reaction of $[Rh_2Cl_2(\mu\text{-CH}_2)(\mu\text{-HFB})(dppm)_2]$ with PMe_3 results in the loss of dppm but not the alkyne ligand, and yields the alkyne-bridged species $[Rh_2Cl(\mu\text{-Cl})(\mu\text{-CH}_2)(\mu\text{-HFB})(PMe_3)_5]$.[20]

Since both metal centres of compound **3** formally have an 18 electron count, the formation of complex **4** is likely initiated by the dissociation of a terminal HFB ligand from **3**. The possibility of at least two intermediate products therefore arises upon CO addition; the observed symmetrical complex **4** and a unsymmetrical compound in which the incoming CO ligand simply replaces the dissociated HFB unit before any rearrangement has occurred. A spectroscopic investigation (Figure 5.3) of the entire reaction mixture, taken after the addition of CO but before the reaction was complete, suggests that such a complex is formed in minor quantities. This second product is tentatively assigned the formula $[Rh_2(CO)_2(\eta^2\text{-HFB})(\mu\text{-HFB})(dmpm)_2]$ (5), and the geometry illustrated below. The $^{31}P\{^1H\}$ NMR resonance assigned to the new species (δ -11.4, multiplet) is a complex multiplet indicating an unsymmetrical configuration. Also consistent with the proposed geometry is the appearance of four separate resonances in the ^{19}F NMR spectrum (Figure 5.3). All are quartets of equal intensity suggesting that each end of the two HFB ligands are in different environments. Based on the appearance of the resonances and the magnitude of the F-F coupling values, the two at δ -47.08 and δ -58.32 ($J_{F\text{-}F}$= 15.9 Hz) have been assigned to the CF_3 groups of the same HFB ligand. Likewise, the two resonances at δ -51.15 and δ -53.64 ($J_{F\text{-}F}$= 12.9 Hz) belong to the second HFB ligand. The infrared spectrum of the reaction mixture reveals two intense terminal CO stretches at 2033 cm^{-1} and 2007 cm^{-1} and two weak bands at 1776 cm^{-1} and 1590 cm^{-1} which are attributed to C=C stretches. The frequencies of the latter two bands are consistent with one terminally bound HFB and one bridging HFB ligand,



5

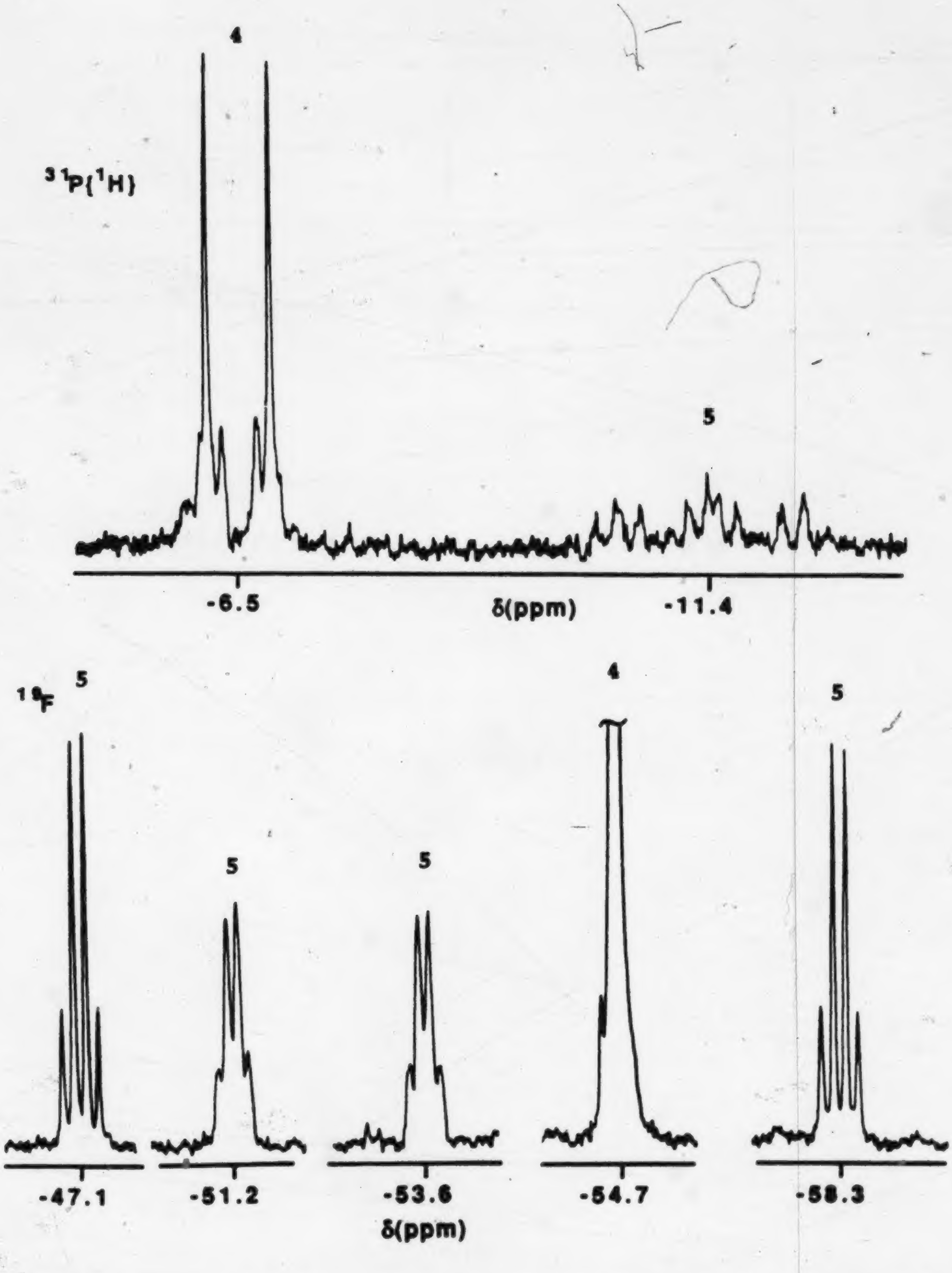


Figure 5.3. The $^{31}P\{^1H\}$ NMR spectrum (top) and the corresponding ^{19}F NMR spectrum (bottom) of $[Rh(CO)(\mu\text{-HFB})(dmpm)]_2$ (4) and $[Rh_2(CO)_2(\eta^2\text{-HFB})(\mu\text{-HFB})(dmpm)_2]$ (5).

the former having more multiple-bond character than the latter. The apparent rearrangement of complex **5** to the symmetrical **4** is borne out in the relatively clean spectra obtained of the final reaction mixture, showing only the presence of **4** and a very minor quantity of impurities.

Migration of an η^2-HFB ligand in complex **5** to a bridged position in complex **4** is interesting from the point of view that η^2-alkyne intermediates have been proposed but never observed for the addition of alkynes to complexes such as $[Ir_2(CO)_2(\mu\text{-}Cl)(dppm)_2][BF_4]$ which immediately generates the cis-dimetalated olefin species $[Ir_2Cl(CO)_2(\mu\text{-alkyne})(dppm)_2][BF_4]$ (alkyne= DMAD, HFB).[12e] This type of rearrangement has also been reported for the binuclear iridium system involving $[Ir_2(CO)_2(\eta^2\text{-HFB})(P(O\text{-}t\text{-}Bu)_3)_2(\mu\text{-}S\text{-}t\text{-}Bu)_2]$.[52] In contrast, attempts to induce the rearrangement of HFB in $[Ir_2(CO)(\eta^2\text{-HFB})(\mu\text{-}S)(\mu\text{-}CO)(dppm)_2]$ [18] were unsuccessful, presumably owing to the inflexibility inherent in the system in which the bridging sulfide and diphosphine ligands do not readily move from their bridging positions. The conversion of compound **5** to complex **4** confirms that this type of rearrangement is possible in bridged-diphosphine dimers.

As yet the DMAD analogue of **3**, $[Rh(\eta^2\text{-DMAD})_2(\mu\text{-}CO)(\mu\text{-DMAD})(dmpm)_2]$, has not been prepared. The addition of excess DMAD (ca. 30 molar equiv) to an ethanol solution of $[Rh_2(CO)_2(\mu\text{-DMAD})(dmpm)_2]$ leads only to the bis(alkyne) species **1**. We interpret these results to mean that DMAD does not interact strongly enough with the rhodium atoms in the starting complex to displace a CO ligand, as in the reaction with HFB. This can be rationalized in terms of a less electronegative DMAD ligand (relative to HFB) [50] which induces less π-backbonding and therefore a weaker interaction from the rhodium atoms. Similar arguments have been used to explain the trend in reactivity of the A-frame complexes [Rh_2X_2(μ-L)(μ-alkyne)$(dppm)_2$] (X= Cl; L= CO, SO_2; alkyne= DMAD, HFB and X= I; L= CO, SO_2; alkyne= HFB) [12f] and the facile loss of DMAD from [$Ir_2(CO)_2$(η^2-DMAD)(μ-S)(μ-CO)$(dppm)_2$].[18]

Conclusions

The utility of "$Rh_2(dmpm)_2$" chemistry to provide new types of binuclear diphosphine complexes has been realized in the preparation of the bis(alkyne) species [Rh(CO)(μ-DMAD)(dmpm)$]_2$ (1), [$Rh_2(CO)_2$-(μ-DMAD)(μ-HFB)$(dmpm)_2$] (2) and [Rh(CO)(μ-HFB)(dmpm)$]_2$ (4) and the tris(alkyne) species [Rh(η^2-HFB$)_2$(μ-CO)(μ-HFB)$(dmpm)_2$] (3). In comparison, the related "$Rh_2(dppm)_2$" and "$Ir_2(dppm)_2$" systems prepared so far have shown no tendency to form such species. The variation in reactivity between dmpm and dppm systems is attributed to the difference in ligand basicity, which produces a build up of electron density at the metal centres and the small steric bulk of dmpm, which allows more room for rearrangement and ligand coordination at the metal centres. The results of this Chapter suggest that size is the most important parameter in allowing a second electrophilic alkyne to be coordinated into the "$Rh_2(dmpm)_2$" complex since the related electron-rich complex [$Ir_2(CO)_2$(η^2-μ-DMAD)$(dppm)_2$] shows no tendency to coordinate a second activated alkyne. Like the monoalkyne-dppm species, the bridged alkyne moieties in the newly prepared bis(alkyne) complexes are not labile towards substitution or subsequent rearrangement, reflecting the inherent stability of the cis-dimetalated olefin form of alkyne coordination.

The structural curiosity of these bis(alkyne) compounds stems from the incorporation of two alkyne molecules and the two Rh atoms into an equatorial plane. The trans geometry of the alkyne ligands is presumably related to the site of alkyne attack at the starting material $[Rh_2(CO)_2$-(μ-alkyne)$(dmpm)_2]$ (alkyne= DMAD, HFB). Other examples of bis(alkyne) species such as $[Ir(\mu\text{-HFB})(NO)(PPh_3)]_2$ [40] contain alkynes as the only bridging ligands and appear to be much less rigid.

Like the related complex $[Ir_2(CO)(\eta^2\text{-HFB})(\mu\text{-S})(\mu\text{-CO})(dppm)_2]$,[18] the preparation of $[Rh(\eta^2\text{-HFB})_2(\mu\text{-CO})(\mu\text{-HFB})(dmpm)_2]$ (3) provides evidence for the initial terminal coordination of alkyne ligands to a metal centre in their reaction with binuclear diphosphine complexes. The subsequent migration of a terminal η^2-HFB ligand in $[Rh_2(CO)_2(\eta^2\text{-HFB})(\mu\text{-HFB})$-$(dmpm)_2]$ (5) into a bridge configuration to yield $[Rh(CO)(\mu\text{-HFB})(dmpm)]_2$ (4) confirms that such rearrangements are possible about a binuclear diphosphine framework.

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Chapter 6

Halide Substitution in Bis(diphenylphosphino)methane-Bridged Rhodium-Iridium Complexes

Introduction

Several approaches can be used to modify the reactivity at a metal centre. Most commonly this is achieved by changing the ancillary ligands and using their differing electronic properties or steric bulk to affect the behaviour of the complex. As shown in Chapters 2-5, substitution of dmpm for the larger, less basic dppm ligand in "Rh_2(diphosphine)$_2$" complexes favours the coordination of a greater number of π-acid ligands and allows more facile ligand rearrangements over the two metal centres.

A more drastic method of modifying the reactivity of bimetallic complexes is to change one of the metals and use the differing properties of each in a cooperative manner to provide patterns of reactivity which have not been observed in homobimetallic systems. The two metals may be either from the same triad or otherwise closely related [1-8] or they may be widely divergent and from opposing ends of the transition metal series.[2,9,10] We were interested in preparing dmpm-bridged rhodium-iridium complexes as a means of advancing our studies of bimetallic-dmpm species, particularly with respect to observing the effects that changing one of the metal centres would have on their reactivity. Our efforts to synthesize such complexes via a route analogous to that used previously for related compounds of dppm,[2,11] were unsuccessful. This was primarily due to our inability to prepare the mononuclear species

$[Ir(CO)(\eta^2\text{-dmpm})_2][Cl]$ which we had intended to use as a precursor for the preparation of dmpm-bridged, binuclear mixed-metal complexes. We therefore turned our attention to the known "$RhIr(dppm)_2$" system which was first reported by Shaw and coworkers [2] and since has been investigated by Mague [3] as well as by our own group.[8,11-14] The purpose of our study was twofold. Firstly, we were interested in obtaining the mixed-metal dppm-bridged analogues of the alkyne-bridged species $[Rh_2(CO)_2(\mu\text{-DMAD})(dmpm)_2]$ and $[Rh_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ in which the metals are in the zero oxidation state. This would allow us to compare the behaviour of the two systems in regards to the coordination of additional activated alkyne molecules, discussed in Chapter 5 for the "$Rh_2(dmpm)_2$" system. Secondly, and more generally, we wanted to determine the effect that replacement of the chloride by the better π-donor iodide ligands would have on the chemistry of complexes such as $[RhIrCl_2(CO)_2(dppm)_2]$. In previous mononuclear compounds such a change was found to have dramatic effects on the binding of the π-acid ligands ethylene and dioxygen.[15,16]

Herein is described the attempted chemical reduction of the mixed-metal complexes $[RhIrCl_2(CO)_2(\mu\text{-HFB})(dppm)_2]$ and $[RhIrCl_2(CO)_2(\mu\text{-DMAD})(dppm)_2]$. The preparation of the iodide complexes $[RhIrI_2(CO)_2(dppm)_2]$ and $[RhIr(CO)_2(\mu\text{-I})(dppm)_2][BF_4]$ and their reactivity with carbon monoxide and dimethyl acetylenedicarboxylate are also described. The interpretation of the $^{13}C\{^1H\}$ NMR spectra of the resulting alkyne species and the implications regarding reassignment of the configuration of the related chloro species $[RhIrCl_2(CO)(\mu\text{-CO})(\mu\text{-DMAD})\text{-}$

$(dppm)_2]$ and $[RhIrCl(CO)_2(\mu\text{-}CO)(\mu\text{-}DMAD)(dppm)_2][ClO_4]$ [3] are discussed.

Experimental

General Comments. General experimental conditions are as described in Chapter 2. Carbon monoxide (C. P. grade) was purchased from Matheson, ^{13}CO (99%) from Isotec Inc., silver tetrafluoroborate ($AgBF_4$), lithium triethylborohydride ($LiBEt_3H$) and dimethyl acetylenedicarboxylate (DMAD) from The Aldrich Chemical Company, sodium borohydride ($NaBH_4$) from Anachemia and potassium iodide (KI) from BDH Chemicals. These and all other reagents were used as received. The complexes $[RhIrCl_2(CO)_2(dppm)_2]$,[2,11] $[RhIr(CO)_3(dppm)_2]$[12] $[RhIrCl_2(CO)_2(\mu\text{-}HFB)(dppm)_2]$ [8] and $[RhIrCl_2(CO)_2(\mu\text{-}DMAD)(dppm)_2]$ [8] were prepared by the reported procedures. All physical measurements were carried out as described in Chapter 2.

Preparation of Compounds (a). $[RhIrI_2(CO)_2(dppm)_2]$ (1). A mixture of $[RhIrCl_2(CO)_2(dppm)_2]$ (250 mg, 0.21 mmol) and 10 equiv of KI (350 mg, 2.10 mmol) were reacted in 10% MeOH/90% CH_2Cl_2 (20 mL) under N_2 for 2 h. Over this time period the orange slurry changed to a brown solution. The solvent was removed under vacuum and the product redissolved in CH_2Cl_2 (25 mL). The brown solution was filtered under N_2 through a pad of celite, the volume reduced to ca. 12 mL under vacuum and diethyl ether (30 mL) was added. Upon cooling to 0°C and allowing the solid to settle, the solvents were removed by cannula under positive N_2 pressure, the brown powder dried under a stream of N_2 and collected in 69% yield (199 mg). Complex **1** was found to be a nonelectrolyte in acetonitrile

($\Lambda(10^{-4}M)$= 7 Ω^{-1} cm^2 mol^{-1}). Anal. Calcd for $C_{52}H_{44}I_2O_2P_4IrRh$: C, 45.5%; H, 3.2%; I, 18.5%. Found: C, 45.0%; H, 3.2%; I, 18.6%.

(b) [RhIr(CO)$_2$(μ-I)(dppm)$_2$][BF$_4$] (2). A solution of $AgBF_4$ (14.2 mg, 0.073 mmol) in THF (5 mL) was added to [RhIrI$_2$(CO)$_2$(dppm)$_2$] **(1)** (100 mg, 0.073 mmol) in 10 mL of THF and the slurry stirred for 1 h. The red-brown solution was filtered through a pad of celite and the volume reduced to ca. 7 mL under vacuum. Diethyl ether (20 mL) was added and the mixture cooled to 0°C to precipitate the product. The solvents were removed by cannula under positive N_2 pressure, the red-brown solid was recrystallized from THF/diethyl ether and then collected in 60% yield (58 mg). Complex **2** was found to be a 1:1 electrolyte in acetonitrile ($\Lambda(10^{-3}M)$= 152 Ω^{-1} cm^2 mol^{-1}). Anal. Calcd for $BC_{52}F_4H_{44}IO_2P_4IrRh$: C, 46.8%; H, 3.3%; I, 9.5%. Found: C, 46.9%; H, 3.4%; I, 8.9%.

(c) [RhIr(CO)$_2$(μ-I)(μ-CO)(dppm)$_2$][I] (3a). A stream of CO was passed through a slurry of [RhIrI$_2$(CO)$_2$(dppm)$_2$] **(1)** (50 mg, 0.036 mmol) in THF (4 mL) for 1 min. Stirring was continued for an additional 5 min, over which time the solution turned yellow, followed by the precipitation of a yellow solid after 10 min. The solvent was removed by evaporation under a stream of CO, the yellow solid was recrystallized from CO-saturated CH_2Cl_2/diethyl ether and collected in 80% yield (41 mg). Complex **3** slowly lost CO when placed under an N_2 atmosphere. It was found to be approximately a 1:1 electrolyte in acetonitrile ($\Lambda(10^{-3}M)$= 105 Ω^{-1} cm^2 mol^{-1}).

(d) [RhIr(CO)$_2$(μ-I)(μ-CO)(dppm)$_2$][BF$_4$] (3b). A solution of [RhIr(CO)$_2$(μ-I)(dppm)$_2$][BF$_4$] **(2)** in THF (15 mL) was prepared as described above using [RhIrI$_2$(CO)$_2$(dppm)$_2$] (**1**) (50 mg, 0.036 mmol). A stream of CO was passed through the solution for 1 min and stirring was continued for 5 min. The solvent was removed by evaporation under a stream of CO, the yellow solid was recrystallized from CO-saturated CH$_2$Cl$_2$/diethyl ether and collected in 62% yield (31 mg).

(e) [RhIr(CO)$_2$(μ-I)(μ-DMAD)(dppm)$_2$][BF$_4$] (4). A solution of [RhIr(CO)$_2$(μ-I)(dppm)$_2$][BF$_4$] (**2**) in THF (10 mL) was prepared as described above using complex **1** (70 mg, 0.051 mmol). After stirring for 1 h, 1.1 equiv of DMAD (6.9 mL, 0.056 mmol) was added directly to the reaction mixture and the stirring was continued for an additional 2 h. The solvents were then removed under vacuum, the residue redissolved in CH$_2$Cl$_2$ (10 mL) and the solution filtered through a pad of celite. Upon stirring overnight, the dark solution turned to clear orange. A more complete conversion to the final product was effected by adding a two-fold excess of DMAD and extending the reaction time to 2-3 days. The solvent was reduced to ca. 4 mL under vacuum, diethyl ether (20 mL) was added and the mixture cooled to 0°C to precipitate a brown-yellow solid. After removing the solvents via cannula under positive N$_2$ pressure, the solid was dried under a stream of dinitrogen. Compound **4** was collected in 64% yield (48 mg). Anal. Calcd for BC$_{58}$F$_4$H$_{50}$IO$_6$P$_4$IrRh: C, 47.2%; H, 3.4%; I, 8.6%. Found: C, 46.9%; H, 3.3%; I, 8.7%.

(f) [RhIrI(CO)$_2$(μ-CO)(μ-DMAD)(dppm)$_2$][BF$_4$] (5). The compound [RhIr(CO)$_2$(μ-I)(μ-DMAD)(dppm)$_2$] (**4**) was prepared as described above from [RhIrI$_2$(CO)$_2$(dppm)$_2$] (**1**) (50 mg, 0.036 mmol) and then redissolved in CH$_2$Cl$_2$. A stream of CO was passed through the solution until a very slight change in colour of the solution to lighter orange occurred (ca. 30 s). The solvents were removed by evaporation under a stream of CO and the product stored under a CO atmosphere. Compound **5** was characterized in CO-saturated solvent (CH_2Cl_2 for infrared or CD_2Cl_2 for ^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ and $^{13}C\{^1H\}\{^{31}P\}$ NMR spectra).

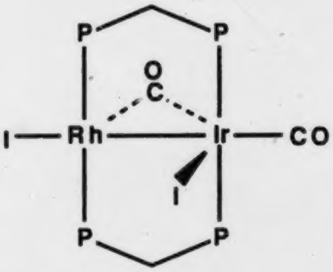
General reaction conditions for the attempted reduction of [RhIrCl$_2$(CO)$_2$(μ-HFB)(dppm)$_2$] and [RhIrCl$_2$(CO)$_2$(μ-DMAD)(dppm)$_2$]. A slurry of either [RhIrCl$_2$(CO)$_2$(μ-HFB)(dppm)$_2$] or [RhIrCl$_2$(CO)$_2$(μ-DMAD)(dppm)$_2$] (50 mg) was prepared in THF (5 mL). A solution of excess $NaBH_4$ (2 molar equiv) in THF (5 mL) was added to the solution of the complex and the mixture was stirred for up to 1 h. For reactions with $LiBEt_3H$, the reagent was added directly to a solution of the complex and the mixture was allowed to stir for up to 1 h. Reactions with Na/Hg amalgam (2 equiv) were carried out in THF solution for up to 3 days. The resulting mixtures were filtered through a pad of celite and the solvent removed under vacuum. The $^{31}P\{^1H\}$ NMR and solution infrared spectra were obtained upon dissolution of the residues in THF.

Results and Discussion

Attempts to prepare the reduced species [RhIr(CO)$_2$(μ-HFB)(dppm)$_2$] or [RhIr(CO)$_2$(μ-DMAD)(dppm)$_2$] from the reaction of [RhIr(CO)$_3$(dppm)$_2$] with DMAD[14] or HFB or the reaction of [RhIrCl$_2$(CO)(μ-CO)(μ-HFB)(dppm)$_2$] or [RhIrCl$_2$(CO)(μ-CO)(μ-DMAD)(dppm)$_2$] with $NaBH_4$, $LiBEt_3H$ or Na/Hg amalgam yielded a number of products, only one of which was successfully identified and shown to be the previously characterized

[RhIr(CO)$_3$(dppm)$_2$].[12] Due to the complexity of the reaction mixture and the difficulty encountered in separating the remaining species, this investigation was not completed. Instead, our efforts were focused on the preparation of the following iodide complexes.

The preparation of [RhIrI$_2$(CO)$_2$(dppm)$_2$] (**1**) is effected from the metathetical reaction between KI and [RhIrCl$_2$(CO)$_2$(dppm)$_2$]. The $^{31}P\{^1H\}$ NMR spectrum of complex **1** is shown in Figure 6.1 (see also Tables 6.1 and 6.2). Two sets of complex multiplets appear, one each for the chemically equivalent phosphorus atoms on rhodium (δ 19.7) and iridium (δ -9.95). The rhodium-bound phosphorus nuclei are readily identified by the additional spin-spin coupling to the ^{103}Rh nucleus ($^1J_{P\text{-}Rh}$= 119.7 Hz). This pattern is consistent with an AA'BB'X spin system and the two resonances have the typical appearance associated with "RhIr(dppm)$_2$" complexes.[3,11-13] The configuration which is illustrated below is based on



1

that determined by crystallographic means for the related species [Ir$_2$I$_2$(CO)$_2$(dppm)$_2$].[8] Although the related compounds [RhIrCl$_2$(CO)$_2$-(dppm)$_2$] and [Ir$_2$I$_2$(CO)$_2$(dppm)$_2$] are reported to be fluxional in solution [8] we see no evidence to suggest similar behaviour from compound **1**.

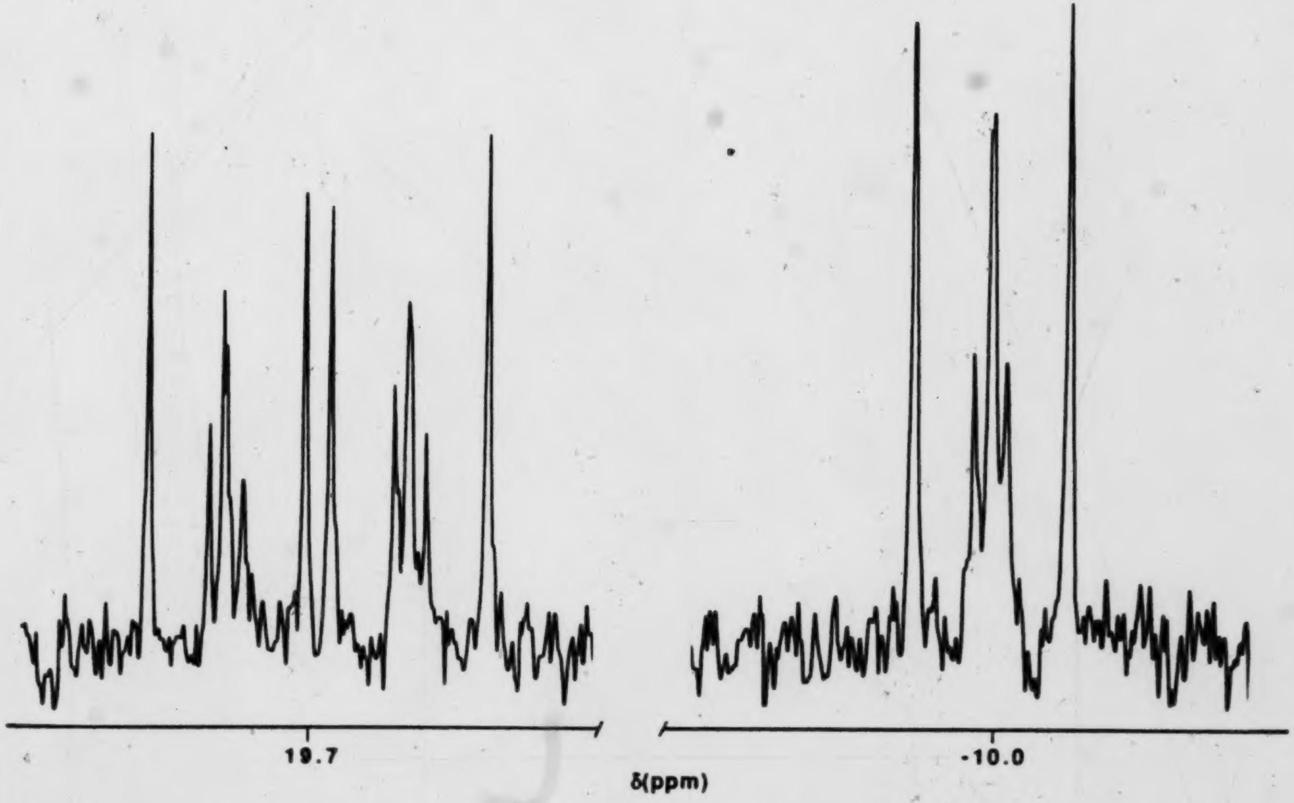


Figure 6.1. The $^{31}P\{^{1}H\}$ NMR spectrum of $[RhIrI_2(CO)_2(dppm)_2]$ (1) at 25°C.

Table 6.1. Infrared Spectroscopic Data for the Compounds in Chapter 6.[a]

		Nujol, cm^{-1}		CH_2Cl_2 solution, cm^{-1}	
no.	compound	ν(CO)	ν(CC)	ν(CO)	ν(CC)
1	$[RhIrI_2(CO)_2(dppm)_2]$	1970(s), 1954(vs, br), 1763(s)		1959(s), 1777(m) 1954(s),[b] 1780(m)[b]	
2	$[RhIr(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]$	1970(m, br), 1948(m, br)		1978(s),[b] 1960(s)[b]	
3 a	$[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][I]$	1963(vs, br), 1827(s)		1984(vs, br), 1848(m) 1939(vs),[c] 1807(m)[c]	
3 b	$[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][BF_4]$	1961(s, br), 1827(m)		1985(vs), 1850(m)	
4	$[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}DMAD)(dppm)_2][BF_4]$	2020(m, sh), 1997(vs), 1703(m)[d]	1588(w)	2031(m, sh), 2008(vs), 1705(m, br)[d]	1587(w)
5	$[RhIrI(CO)_2(\mu\text{-}CO)(\mu\text{-}DMAD)(dppm)_2][BF_4]$	2089(s), 2055(vs), 1738(s), 1712(s)[d], 1697(s)[d]	1577(w)	2091(m), 2059(s), 1748(m) 1707(m)[d]	1573(w)

[a] Abbreviations used: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad. [b] THF solution.

[c] ν(^{13}CO). [d] ν(CO_2Me).

Table 6.2. NMR Spectroscopic Data for the Compounds in Chapter 6.[a, b]

	$^{31}P\{^1H\}^c$			$\delta(^{13}C\{^1H\})^d$	$\delta(^1H)$		
no	δ (P_{Rh})	δ (P_{Ir})	$^1J_{Rh-P}$, Hz		P-CH_3	-CH_2-	-OCH_3
1	19.7	-9.95	119.7		7.4(m, 40H)	4.59(m, 4H)	
2	19.7	15.8	125.9		7.5(m, 40H)	2.53(m, 4H)	
3 a	26.1	-6.0	95.7	197.3(dm, $^1J_{C-Rh}$= 34.7 Hz),	7.4(m, 40H)	4.74(m, 2H),	
				191.1(dm, $^1J_{C-Rh}$= 78.7 Hz),		4.33(m, 2H)	
				177.4(qr, $^2J_{C-P}$= J= 13 Hz)			
3b	25.6	-6.2	96.0		7.4(m, 40H)	4.4(m, 4H)	
4	16.1	-13.6	89.1	186.9(ddt, $^1J_{C-Rh}$= 64.0 Hz,	7.4(m, 40H)	4.1(m, 2H),	3.1(s, 3H),
				$^3J_{C-C}$= 6 Hz),		4.0(m, 2H)	3.0(s, 3H)
				173.8(m, $^3J_{C-C}$= 4 Hz)			
5	18.6	-30.4	131.0	201.4(m, $^1J_{C-Rh}$= 19.5 Hz,	7.4(m, 40H)	4.5(m, 2H),	3.37(s, 3H),
				$^2J_{C-P(Ir)}$ ~ 10 Hz, $^2J_{C-C(Ir)}$= 47.5 Hz),^{e}		2.8(m, 2H)	1.75(s, 3H)
				190.2(dt, $^1J_{C-Rh}$= 53.4 Hz, $^2J_{C-P(Rh)}$= 10.4 Hz)^e			
				157.1(dt, $^2J_{C-P(Ir)}$= 5.8Hz, $^2J_{C(Ir)-C}$= 47.5 Hz),^{e}			

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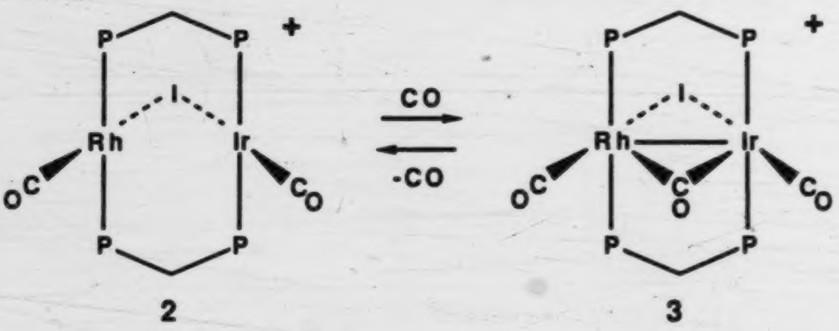
[a] Ambient temperature in CD_2Cl_2 unless otherwise noted. [b] Abbreviations used: s, singlet; qr, quartet; m, multiplet; dt, doublet of triplets; dm, doublet of multiplets; ddt, doublet of doublet of triplets. [c] Vs 85% H_3PO_4, all resonances appear as two (Rh) or one (Ir) second-order, five-line multiplet(s) with three principal peaks. [d] ^{13}CO enriched samples. [e] -40°C.

The proposed geometry of the CO ligands in compound **1** is based on the solution-infrared spectrum which indicates the presence of one terminal (1959 cm^{-1}) and one bridging (1777 cm^{-1}) carbonyl ligand, (see Table 6.1). Since the frequency of the terminal CO ligand in compound **1** matches that of the diiridium analogue $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$ (ν(CO)= 1960, 1742 cm^{-1}, CH_2Cl_2)[8] we believe it to be bound to iridium rather than rhodium. This assignment is consistent with the assumption that iridium, being more basic than rhodium, would interact more strongly with a π-acid CO ligand. The presence of one terminal and one bridging CO ligand rather than two terminal CO ligands in complex **1** can be justified by considering the expected build up of electron density at the metal centres, brought about by the good electron-donor ability of the iodo ligand.[17] Since bridging CO is a better π-acid than terminally bound CO,[18] the former is able to relieve more of the electron density on the metal atoms. In this regard, the conversion of CO ligands from terminal to bridging coordination modes has been observed in the related homobinuclear compound $[Ir_2Cl_2(CO)_2(\mu\text{-}DMAD)(dppm)_2]$ upon substitution of CO for electron donating groups, providing the complexes $[Ir_2Cl_2L(\mu\text{-}CO)(\mu\text{-}DMAD)(dppm)_2]$ (L= PMe_3, $P(OMe)_3$, NCMe).[19]

The overall configuration of compound **1** is assumed to involve sixteen-electron rhodium and eighteen-electron iridium metal centres. This same geometry has been confirmed by X-ray crystallography for the diiridium analogue of **1**, $[Ir_2I_2(CO)(\mu\text{-}CO)(dppm)_2]$,[8] and the related complex $[Rh_2Cl_2(CO)(\mu\text{-}CO)\{(MeO)_2PN(Et)P(OMe)_2\}_2]$,[20] and has been proposed for other similar species including $[RhIrCl_2(CO)_2(dppm)_2]$.[8] In general, the sixteen-electron rhodium, eighteen-electron iridium configuration appears to be the favoured geometry of "$RhIr(dppm)_2$" complexes.[3,8,11-13]

In solution, the possibility of iodide dissociation from compound **1** to form a cationic isomer containing two sixteen-electron metal centres seems remote since conductivity measurements carried out in acetonitrile ($\Lambda(10^{-4}M) \sim 7\ \Omega^{-1}\ cm^2\ mol^{-1}$) indicate that the species is a nonelectrolyte. However, in the solid state, the appearance of three bands in the infrared spectrum (1970(s), 1954(vs, br) and 1763(s) cm^{-1}) raises the possibility of two geometrical forms, one of which could very well be an ionic species. Following the discussion above, the two bands appearing at 1954 and 1768 cm^{-1} can be attributed to the neutral configuration observed in solution. If it is then assumed that in the solid state spectrum, the 1954 cm^{-1} band of the neutral species is coincidentally overlapping a second band which is due to this additional species (an assumption which is suggested by the broadness of the band) we can assign the two bands at 1970 and 1954 cm^{-1} to the additional species. The similarity in frequency of these two terminal bands with those of the A-frame species $[RhIr(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]$ (**2**) ($\nu(CO)$= 1970(m), 1948(m) cm^{-1}, see Table 6.1) suggests that an iodide ligand has dissociated to form an ionic A-frame complex, $[RhIr(CO)_2(\mu\text{-}I)\text{-}(dppm)_2][I]$. The stabilization of such a species by ion-ino interactions in the solid state may account for the observance of only the neutral form of **1** in solution. Since the related complexes $[Rh_2X(CO)(\mu\text{-}CO)(dppm)_2][X]$ (X= Br, I) have been prepared by similar means from the reactions of NaBr and KI with *trans*-$[RhCl(CO)(dppm)]_2$ [21] it seems quite likely that an ionic mixed-metal species could be produced in the above reaction. Other forms of compound **1**, including the neutral face-to-face dimer, seem an unlikely prospect in light of the propensity for both the homo- and heterobimetallic analogues of **1** to be unsymmetrical complexes.[11,21]

The mixed-metal species $[RhIr(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]$ (**2**) is prepared from the reaction of 1 equiv of $AgBF_4$ with complex **1** in THF solution. All spectroscopic data are consistent with the familiar homobimetallic A-frame geometry[22-25] (see Tables 6.1 and 6.2) in which the iodide ligand is situated in a bridging position at the apex of the letter "A". Two bands, appearing at 1970 and 1948 cm^{-1} (Nujol) in the infrared spectrum of **2**, are attributed to the terminally bound CO ligands. Both bands are at lower frequencies than those of the chloride analogue $[RhIr(CO)_2(\mu\text{-}Cl)\text{-}(dppm)_2][BF_4]$, ($\nu$(CO)= 1993, 1974 cm^{-1}, Nujol),[8] a consequence, no doubt, of the greater π-donor ability of iodide over chloride and the resulting increased electron density at the metal centers of the iodide complex.[17]



The reaction of compound **1** with CO yields a single product which, upon characterization by spectroscopic means (see Tables 6.1 and 6.2), was determined to be $[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][I]$ (**3a**). The doubly-bridged

A-frame geometry proposed for **3a** has been observed for related homobinuclear diphosphine compounds[21,23,24a,24b,26,27] and was also proposed for the diiridium analogue $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][I]$.[8] The implied dissociation of iodide from **1** upon CO addition was verified by conductivity measurements, with an acetonitrile solution of the final complex having a conductance of 105 Ω^{-1} cm^2 mol^{-1}. Although this value is outside the range generally accepted for a 1:1 electrolyte in acetonitrile (120 - 160 Ω^{-1} cm^2 mol^{-1}),[28] it is significant and it represents a considerable increase in conductance from that of the starting material ($\Lambda(10^{-4}$ M) ~ 7 Ω^{-1} cm^2 mol^{-1} for complex **1**). The lower than expected conductance is presumed to be a consequence of strong ion pairing within the complex.

The $^{31}P\{^1H\}$ NMR spectrum of compound **3a** reveals resonances much like those observed for compound **1** only with somewhat different chemical shifts ($\delta(P_{Rh})$ 26.1, $^1J_{P\text{-}Rh}$= 125.9 Hz; $\delta(P_{Ir})$ -6.0). The infrared spectrum displays only one terminal carbonyl stretch ($\nu(CO)$= 1963 cm^{-1}) but from the width of this band we infer that the second terminal CO band is coincidently overlapped by the first. The remaining CO stretch appears at a frequency ($\nu(CO)$= 1827 cm^{-1}) consistent with a bridging CO ligand. The $^{13}C\{^1H\}$ NMR spectrum of **3a** contains three complex multiplets in the carbonyl region all of which appear unresolved due to numerous spin-spin coupling sources. Their individual assignment is made possible by the distinctive downfield shift of bridging CO relative to terminal CO and the additional splitting of the signals resulting from coordination to rhodium. The trend of lower field chemical shifts for bridging carbonyl ligands is widespread among "MM'(diphosphine)$_2$" complexes (M=

M'=Rh, Ir; M= Rh, M'= Ir) found in this thesis and elsewhere.[3,8,14,22,27,29] Hence, the resonance at δ 197.3 is assigned to the bridging CO ligand. The spin-spin coupling magnitude of 34.7 Hz is typical of a one-bond interaction of the carbon atom of bridging CO with rhodium.[3,14,27,30,31] The terminally coordinated CO's appear as a multiplet at $\delta(P_{Rh})$ 191.1 ($^1J_{C\text{-}Rh}$= 78.7 Hz) and an apparent quartet at $\delta(P_{Ir})$ 177.4 ($^2J_{C\text{-}P}$= 13 Hz, J= 13 Hz). The iridium-bound CO is best described as an overlapped doublet of triplets resulting from coupling to two chemically equivalent phosphorus nuclei and an unknown source, possibly the rhodium metal centre or the bridging CO ligand. The remaining spin-spin coupling values could not be obtained due to the complex nature of the multiplets. Phosphorus-decoupling the spectrum should help to identify this unknown source, however, at the time this compound was chararterized, the {^{31}P} feature was not available and the spectrum has yet to be recorded.

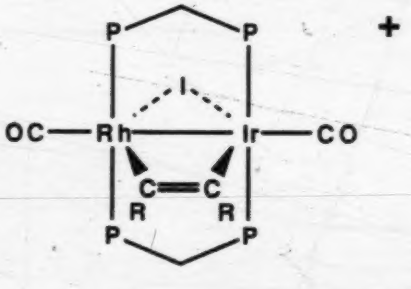
The exposure of a solution of compound **2** to CO yields $[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][BF_4]$ (**3b**), the BF_4^- analogue of **3a**. The similarities in both complexes is evident from the close agreement between their spectroscopic data (Tables 6.1 and 6.2) and much of the discussion of **3a** can also be applied to **3b**. One notable exception is the conductivity of **3b** ($\Lambda(10^{-3}$ M)= 152 Ω^{-1} cm^2 mol^{-1}) which is well within the acceptable range for a 1:1 electrolyte in acetonitrile.[28] The disparity in values between **3a** and **3b** is attributed to the stronger ion pairing of the I^- ion compared BF_4^-.[32] Both iodide complexes readily lose CO, regenerating the dicarbonyl starting material, and neither shows any sign of forming a tetracarbonyl product as was observed with the diiridium iodo and rhodium-iridium chloro analogues.[8]

Upon comparing the related homo- and heterobinuclear rhodium and iridium systems with the above, it is found that complex **1** behaves much like the diiridium analogue $[IrI(CO)(dppm)]_2$ [8] upon reaction with CO, both producing cationic tricarbonyl species having similar geometries. In contrast, the dichloride complexes *trans*-$[IrCl(CO)(dppm)]_2$ [30] and $[RhIrCl_2(CO)_2(dppm)_2]$ [8] initially coordinate a third CO ligand without Cl^- dissociation and then subsequently form tetracarbonyl species upon Cl^- loss. Using the same arguments presented for the $[IrI(CO)(dppm)]_2$ system,[8] the difference in behaviour between the mixed-metal chloride and iodide complexes is attributed to the greater steric demands of the iodo ligand which enhances iodide dissociation upon CO addition. Steric crowding also accounts for the lack of any tetracarbonyl products in either of the iodide systems since the presence of a better π-donor I^- should favour complexes with a greater number of carbonyl ligands.

The reactions of DMAD with $[RhIrI_2(CO)_2(dppm)_2]$ (**1**) and $[RhIr(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]$ (**2**) were studied to see if the trend in reactivity of the mixed-metal iodide continued to follow that of their diiridium counterparts [8] in the presence of more complex ligands than carbon monoxide. The reaction of compound **1** with DMAD is complicated by the formation of a number of species which we have not characterized. This result in itself is reminiscent of the reaction of $[IrI(CO)(dppm)]_2$ with DMAD which revealed at least four species, all involving rearrangement of a single coordinated DMAD molecule.[8] There was little to be gained by pursuing this chemistry since the species obtained appeared to parallel those of the $[IrI(CO)(dppm)]_2$ system. Therefore, we focused our efforts on the behaviour of compound **2**.

The addition of 1 equiv of DMAD directly to a freshly prepared solution of $[RhIr(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]$ (**2**) in THF results in an initial change in colour of the brown slurry to green, followed by a return of the brown colour within minutes. No further changes were observed upon stirring the solution overnight. A $^{31}P\{^1H\}$ NMR spectrum taken of the reaction mixture reveals the presence of two major species ((i). $\delta(P_{Rh})$ 11.6, $\delta(P_{Ir})$ -21.5, $^1J_{P\text{-}Rh}$= 112 Hz; (ii). $\delta(P_{Rh})$ 16.1, $\delta(P_{Ir})$ -13.6, $^1J_{P\text{-}Rh}$= 89 Hz) both having $^{31}P\{^1H\}$ NMR patterns reminiscent of those illustrated in Figure 6.1. The continued stirring of the mixture for up to two days does not appear to result in any further reaction. However, upon removal of the solvents under vacuum and dissolution of the residue in CH_2Cl_2, the reaction proceeds slowly (2 days) to yield primarily a single species which corresponds to the latter set of $^{31}P\{^1H\}$ NMR resonances listed above.

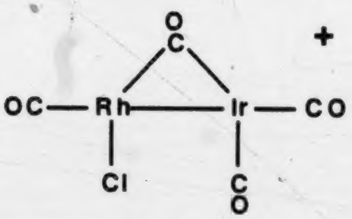
Subsequent characterization of the product by spectroscopic techniques and elemental analysis reveals it to be $[RhIr(CO)_2(\mu\text{-}I)\text{-}(\mu\text{-}DMAD)(dppm)_2][BF_4]$ (**4**), having a structure analogous to that of

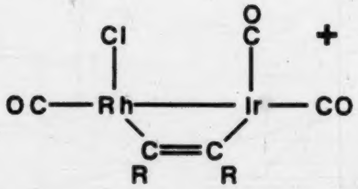


4

$[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}DMAD)(dppm)_2][BF_4]$.[8] The infrared spectrum of **4** contains two terminal carbonyl bands ($\nu(CO)$= 2020, 1997 cm^{-1}, Nujol) which are significantly higher in frequency than those of the starting complex $[RhIr(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]$ ($\nu(CO)$= 1970, 1948 cm^{-1}). This shift is in accordance with a formal oxidation state change of the metal centres from M(I) to M(II). The apparent electronic effect on the complex of replacing an iridium atom in $[Ir_2(CO)_2(\mu\text{-}I)(\mu\text{-}DMAD)(dppm)_2][BF_4]$ ($\nu(CO)$= 1987 cm^{-1}, Nujol) [8] with the presumably less basic rhodium atom of complex **4** is realized in higher frequency carbonyl stretches for the latter. The fact that both carbonyl frequencies of the mixed-metal compound are higher than those of the diiridium complex suggests that in the former, the rhodium atom may have a long range effect on the iridium-bound CO ligand. The presence of such interactions is also indicated by the $^{13}C\{^1H\}$ NMR results, discussed below. As the following discussion implies, the proposed collinear arrangement of CO ligands along the rhodium-iridium axis may favour such effects. Other prominent features of the infrared spectrum of **4** include bands attributed to the coordinated alkyne molecule at 1703 cm^{-1} ($\nu(CO_2Me)$) and 1588 cm^{-1} ($\nu(CC)$). The frequency of the C-C vibration is comparable to related binuclear alkyne complexes in which the alkyne ligand is in a bridging position and is formally considered to be a dianionic, four-electron donor.[3,19,29,33-35] It is assumed that the ligand is coordinated parallel to the metal-metal axis since this is the mode heavily favoured for "MM'(diphosphine)$_2$" complexes (M= M'= Rh, Ir; M= Rh, M'= Ir) involving rhodium and iridium centres.[3,19,29,33,34]

Support for the proposal that both CO ligands are coordinated along the metal-metal axis in **4** as shown, is found in the phosphorus-decoupled ^{13}C{^{1}H} NMR spectrum. The carbonyl region of the undecoupled spectrum shown at the top of Figure 6.2 contains two complex resonances (δ 186.9, doublet of doublet of triplets; δ 173.8, multiplet) which appear unresolved due to numerous spin-spin coupling sources. Broadband phosphorus decoupling the spectrum transforms the downfield resonance into a doublet of doublets (bottom of Figure 6.2). The magnitude of the large coupling (64.0 Hz) clearly establishes the resonance as that belonging to the rhodium-bound CO ligand. The second coupling value (6 Hz) is suggestive of a weak interaction such as a three-bond collinear coupling to the iridium bound CO. Collinear coupling through two and three bonds appears to be quite efficient and and several examples of H*-M-M-H*, H*-M-M*, OC*-M-M* and OC*-M-M-C*O coupling (starred atoms represent spin-coupled nuclei) have been proposed for binuclear complexes.[11,36] Of particular relevance to this study, the complexes [RhIrCl(CO)$_3$(μ-CO)-(dppm)$_2$][Cl] [8] and [RhIrCl(CO)$_3$(μ-CO)(μ-DMAD)(dppm)$_2$][ClO$_4$] [3] having the proposed configurations illustrated below, also show evidence in the ^{13}C{^{1}H} NMR spectra for possible long range OC*-Ir-Rh* and OC*-Rh-Ir-C*O interactions, respectively.





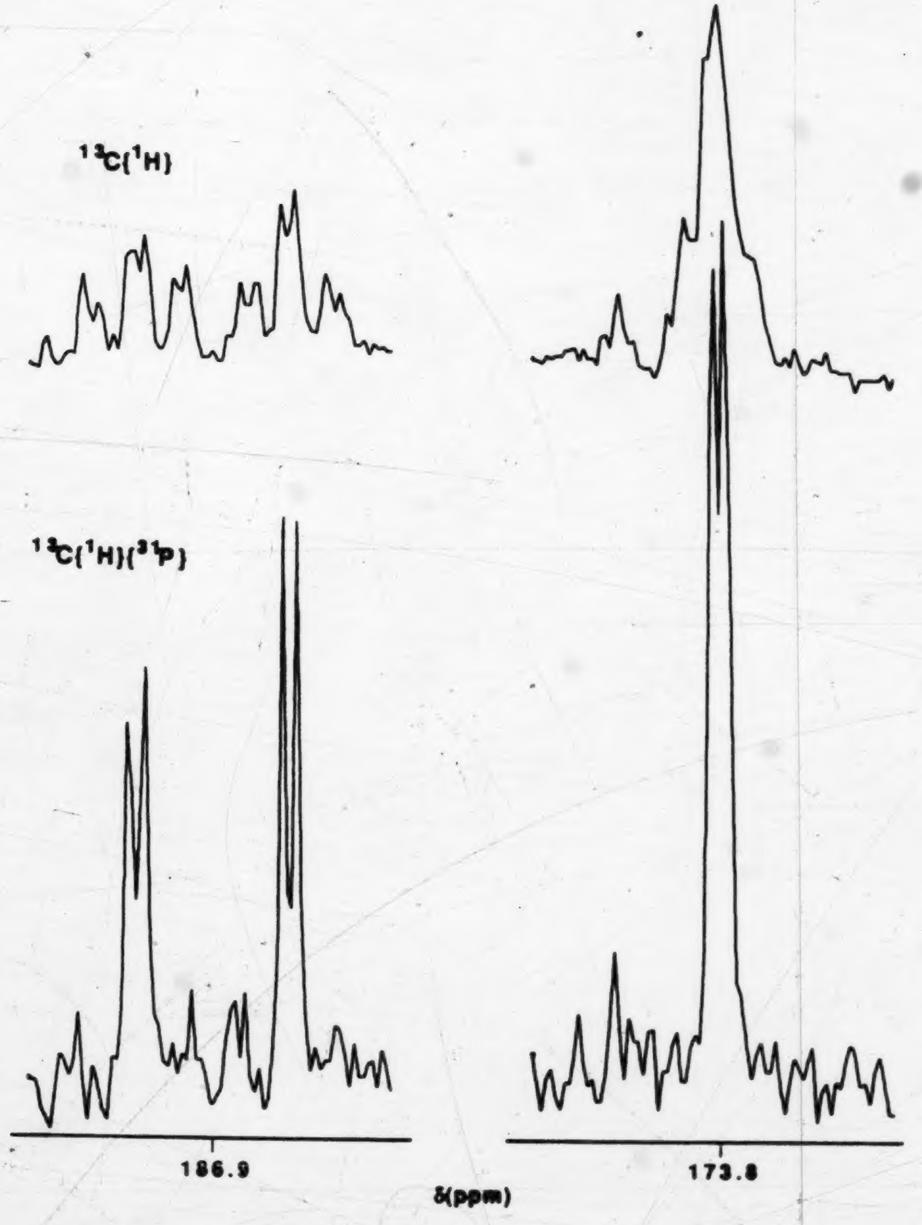
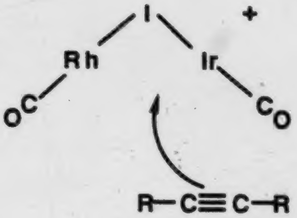


Figure 6.2. The carbonyl region of the $^{13}C\{^1H\}$ and $^{13}C\{^1H\}\{^{31}P\}$ NMR spectra of $[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}DMAD)(dppm)_2][BF_4]$ (4) at 25°C.

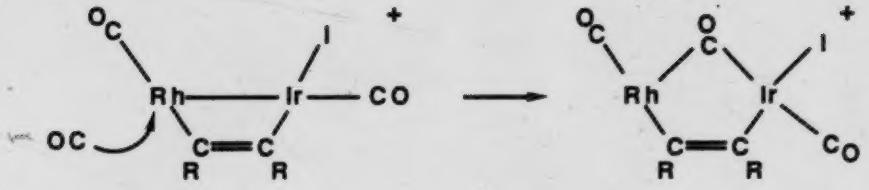
The iridium-bound CO resonance (δ 173.8) of complex **4** exhibits an additional coupling (4 Hz) which is also assigned to a collinear three-bond interaction. Theoretically the value should equal that found for the rhodium-bound CO ligand but the difference is small enough (2 Hz) to be accounted for by the resolution limits of the spectrum or perhaps less efficient decoupling of the iridium-bound phosphorus signal. Other possible coupling sources such as BF_4^- have been discounted on the basis of the normal appearance of the ^{19}F NMR spectra (δ(BF_4) -152.1, singlet, CD_2Cl_2). The collinear proposal ignores the possibility of significant two-bond Rh-Ir-CO coupling although there is no apparent reason why such an interaction should not be present. We note, however, that rhodium coupling is occasionally unobserved in other spectra where longer distance coupling to another nucleus is clearly seen. Such is the case for the ^1H NMR spectrum of the complexes [RhIr(H)(SH)$(CO)_2(dppm)_2$] and [RhIr(H)(SeH)$(CO)_2(dppm)_2$] where coupling between phosphorus and the proton attached to the rhodium-bound sulfhydryl or selenhydryl ligand is observed ($^3J_{H(S)-P}$= 6.4 Hz, $^3J_{H(Se)-P}$= 6.4 Hz) but rhodium coupling with the proton is not observed.[37]

From the above results it can be seen that compound **2** behaves much like [$Ir_2(CO)_2$(μ-I)$(dppm)_2$][BF_4] when reacted with DMAD, in providing a complex containing one CO ligand on each metal centre and both the alkyne and the halide ligands in a bridging mode.[8] As suggested for the diiridium complex, the final configuration of the product **4** implies that the alkyne attacks in the pocket of the A-frame starting material, on the side of the M_2P_4 plane away from the halide ligand. It appears that the large iodide ligand in complex **2** may also sterically inhibit alkyne attack at a site adjacent to the halide. In contrast, the mixed-metal species



$[RhIr(CO)_2(\mu\text{-}Cl)(dppm)_2][BF_4]$, which contains the smaller bridging chloride, reacts with DMAD yielding a product ($[RhIrCl(CO)_2(\mu\text{-}DMAD)\text{-}(dppm)_2][BF_4]$ [8]) which has the halide ligand terminally coordinated to rhodium and both CO ligands bound to iridium. This configuration requires the alkyne molecule to attack the A-frame starting material adjacent to the bridging halide group. The acetate complex $[Rh_2(CO)_2\text{-}(\mu\text{-}O_2CMe)(dppm)_2]^+$ [29,34a] and the sulfide compound $[Ir_2(CO)_2(\mu\text{-}S)\text{-}(dppm)_2]$ [13] also presumably undergo alkyne attack at a site adjacent to the bridging anionic ligand, as shown by the structure of the HFB adduct of the latter species, $[Ir_2(CO)(\eta^2\text{-}HFB)(\mu\text{-}S)(\mu\text{-}CO)(dppm)_2]$.

Complex **4** reversibly adds one equivalent of CO to provide the tricarbonyl species $[RhIrI(CO)_2(\mu\text{-}CO)(\mu\text{-}DMAD)(dppm)_2][BF_4]$ (**5**). We suggest that the reaction proceeds with the movement of the iodide ligand out of a bridging position to form a sixteen-electron rhodium, eighteen-electron iridium species. Carbon monoxide addition to the coordinatively unsaturated rhodium atom takes place, followed by the rearrangement of a rhodium-bound CO ligand into a bridging position. A mechanism very similar to this has been suggested by Mague for the addition of CO to



4 R= CO_2Me 5

[RhIrCl(CO)$_2$(μ-DMAD)(dppm)$_2$][ClO$_4$] which provides the related species [RhIrCl(CO)$_2$(μ-CO)(μ-DMAD)(dppm)$_2$][ClO$_4$].[3] The proposed geometry of compound **5** is consistent with the spectroscopic information (see Tables 6.1 and 6.2) and is based on the sixteen-electron rhodium, eighteen-electron iridium configuration described in several accounts of "RhIr(dppm)$_2$" complexes.[3,8,11-14]

The carbonyl region of the infrared spectrum of **5** is compatible with the presence of two terminally coordinated carbonyl ligands (ν(CO)= 2089, 2055 cm^{-1}) and a single bridging carbonyl (ν(CO)= 1738 cm^{-1}). Bands associated with the alkyne fragment (ν(CO$_2$Me)= 1712, 1697 cm^{-1}; ν(CC)= 1577 cm^{-1}) are of similar frequency to those of the starting complex, **4** (Table 6.1), suggesting, as it has been found previously in Chapter 5, that the alkyne ligand prefers to remain coordinated in a bridged position.

The $^{13}C\{^{1}H\}$ NMR and $^{13}C\{^{1}H\}\{^{31}P\}$ NMR spectra of **5**, illustrated in Figure 6.3, provide valuable information regarding the configuration of the three CO ligands. The easiest of the three signals to identify is that belonging to the rhodium-bound CO which appears at δ 190.2 as a doublet of triplets in the $^{13}C\{^{1}H\}$ NMR spectrum (top of Figure 6.3). The splitting pattern and coupling values are typical of CO coordinated to one rhodium atom ($^{1}J_{C\text{-}Rh}$= 53.4 Hz) and also coupled to two adjacent phosphorus atoms

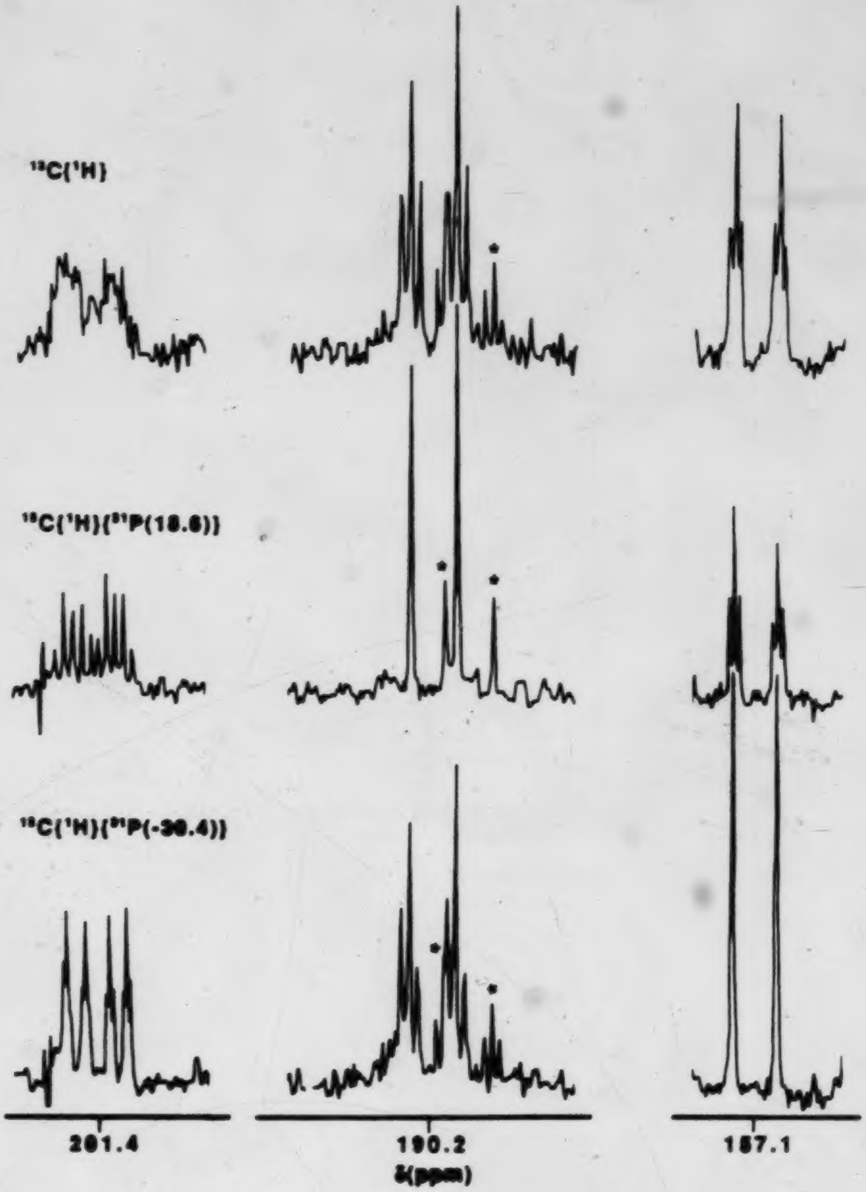
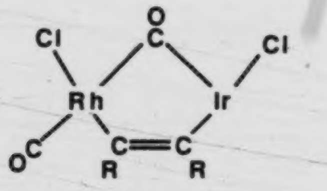


Figure 6.3. The carbonyl region of the $^{13}C\{^1H\}$ and $^{13}C\{^1H\}\{^{31}P\}$ NMR spectra of $[RhIrI(CO)_2(\mu\text{-}CO)(\mu\text{-}DMAD)(dppm)_2][BF_4]$ (5) at -40°C. Peaks due to impurities are marked with an asterisk.

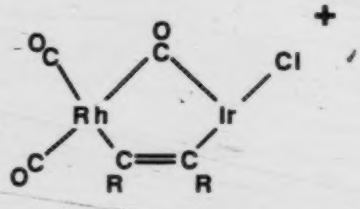
($^2J_{C\text{-}P}$=10.4 Hz).[3,22,27,29,31] Decoupling the rhodium-bound phosphorus nuclei transforms the resonance into a well resolved doublet (middle of Figure 6.3, {^{31}P(18.6)}) while decoupling the iridium-bound phosphorus has no effect (bottom of Figure 6.3, {^{31}P(-30.4)}). The upfield resonance, at δ 157.1, also appears as a doublet of triplets with coupling values of 47.5 and 5.8 Hz. The latter value is consistent with a two-bond C*-M-P* interaction and the larger coupling implies that this particular CO ligand is also directly bound to rhodium. Two points about this assignment are worrisome. First, the chemical shift of the resonance is farther upfield than what is usually observed for rhodium-bound terminal carbonyls and is actually more characteristic of an iridium-bound carbonyl (See Chapters 2 and 4 of this thesis and references 3, 8, 13, 22, 27, 29, 31, 33b and 38 for typical chemical shift values of related compounds). More importantly, decoupling the rhodium-bound phosphorus nuclei (middle of Figure 6.3) has no effect on the resonance (δ 157.1) but decoupling the iridium-bound phosphorus nuclei transforms it into a doublet (bottom of Figure 6.3). Clearly then, the CO ligand in question is bound to iridium. Faced with these results we are forced to conclude that the additional 47.5 Hz coupling arises from a two-bond interaction between the carbon atoms of the terminal CO ligand on iridium and the bridging CO ligand situated trans to it.

Convincing evidence of the proposed trans OC*-Ir-C*O interaction is found upon examining the spectra of the third resonance δ 201.4. Attributed to the bridging carbonyl ligand, the signal appears as a featureless multiplet in the ^{13}C{^{1}H} NMR spectrum. As shown, decoupling each of the rhodium- and iridium-bound phosphorus nuclei in turn affects the resonance, transforming it into a different set of doublet of doublet of triplets in each case. The assigned one-bond C-Rh coupling of 19.5 Hz, obtained from the bottom spectrum, is within the observed range (ca. 19- 45 Hz) for a bridging CO ligand in related "MM'(diphosphine)$_2$" complexes (M= M'= Rh; M= Rh, M'= Ir).[3,8,22,27,29,33a] It is, however, at the lower end of the range suggesting that the interaction is weakened, perhaps by stronger coordination to the iridium atom. Consistent with this proposal, two-bond coupling to the rhodium-bound phosphorus nuclei is too small to be accurately measured (bottom of Figure 6.3) yet two-bond coupling to the iridium-bound phosphorus nuclei (middle of Figure 6.3) is larger, at approximately 10 Hz. The additional splitting of this resonance into a doublet (J= 47.5 Hz) is most apparent in the $^{13}C\{^1H\}\{^{31}P_{Ir}\}$ spectrum (bottom of Figure 6.3). It cannot be accounted for by a rhodium or phosphorus interaction and it matches the additional coupling observed for the terminal iridium-bound carbonyl, suggesting that the two carbon atoms are coupled to each other.

The magnitude of the interaction in question is uncharacteristically large and unfortunately there is little published data with which to directly compare this value. Mague and coworkers have reported values for trans OC*-M-C*O interactions in related binuclear complexes but the largest of these is only ca. 14 Hz.[3,22,27] Although not reported as such, close examination of Mague's work on the [RhIrCl$_2$(CO)$_2$(dppm)$_2$] [3] system does suggest that trans OC*-M-C*O interactions, comparable in magnitude to those of compound 5, do exist. For the most part the report in question deals with complexes which all have the sixteen-electron rhodium, eighteen-electron iridium configuration familiar to such mixed-metal systems.[3,8,11-13] The two exceptions to this are the compounds [RhIrCl$_2$(CO)(μ-CO)(μ-DMAD)(dppm)$_2$] and [RhIrCl(CO)$_2$(μ-CO)(μ-DMAD)-(dppm)$_2$][ClO$_4$] which have been assigned the configurations **A** and **B**, illustrated below. It seems odd that only these two complexes should have a reverse eighteen-electron rhodium, sixteen-electron iridium count. Our



A



B

R= CO$_2$Me

^{13}C{^{1}H} NMR data (CD$_2$Cl$_2$)

δ(μ-CO) 224.1(m)

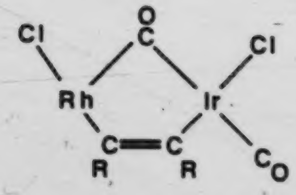
δ(CO) 164.9(dm,$^1J_{C\text{-}Rh}$= 42.0 Hz)

^{13}C{^{1}H} NMR data (CD$_2$Cl$_2$, -53°C)

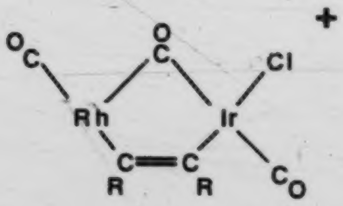
δ(μ-CO) 204.7(m)

δ(CO) 189.2(dt,$^1J_{C\text{-}Rh}$= 54.0 Hz, $^2J_{C\text{-}P}$= 10.2 Hz)

δ(CO) 158.9(dt, $^1J_{C\text{-}Rh}$= 48.0 Hz, $^2J_{C\text{-}P}$= 6.3 Hz)



C



D

attention was drawn to the spectroscopic data of these two complexes, in particular the $^{13}C\{^1H\}$ NMR data which has been reproduced here for convenience. The resonances appearing at δ 164.9 for **A** and δ 158.9 for **B** are assigned to rhodium-bound CO ligands based on the observance of coupling values which are of the correct magnitude for a one-bond Rh^*-C^*O interaction.[31] However, the chemical shifts of both of these resonances are more in line with iridium-bound carbonyls,[3,8,31] especially for the case of **B** where it is within one ppm of the iridium-bound carbonyl shift of complex **5**.

In consideration of the data obtained on complex **5** and the configuration assigned, we propose that **C** and **D** represent a more accurate view of Mague's two chloro complexes. The new configuration of $[RhIrCl_2(CO)(\mu\text{-}CO)(\mu\text{-}DMAD)(dppm)_2]$, represented by **C**, is very similar to that of the dirhodium species $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}DMAD)(dppm)_2]$.[33b] The coupling values of 42 Hz for **A** and 48 Hz for **B**, now attributed to a trans OC^*-Ir-C^*O interaction, are of the same magnitude as that observed for compound **5**. It is unfortunate that in the absence of $^{13}C\{^1H\}\{^{31}P\}$ NMR spectra no coupling values were obtained from the bridging CO resonance with which to confirm the interaction. It is significant that all three carbonyl resonances for Mague's species (now formulated as **D**) are very close to those of compound **5**, for which an analogous structure is proposed.

Summary

The mixed-metal complex $[RhIrI_2(CO)_2(dppm)_2]$ (**1**) shows behaviour which is characteristic of both the "$Ir_2I_2(dppm)_2$" and "$RhIrCl_2(dppm)_2$" analogues in the formation of an unsymmetrical species containing one terminal and one bridging carbonyl ligand. The proposed sixteen-electron rhodium, eighteen-electron iridium configuration of compound **1** is analogous to that which is commonly found in "$RhIr(dppm)_2$" complexes.[3,8,11-13] The subsequent reaction of the compounds $[RhIrI_2(CO)_2(dppm)_2]$ (**1**) and $[RhIr(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]$ (**2**) with CO provides complexes, $[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][I]$ (**3a**) and $[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2][BF_4]$ (**3b**), which are more characteristic of the related "$Ir_2I_2(dppm)_2$" system than "$RhIrCl_2(dppm)_2$".[8] Much of this behavioural difference presumably has to do with the steric limitations imposed on the complex by the large size of the iodide ligand. Thus the cationic tricarbonyl species $[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}CO)(dppm)_2]^+$ (**3**) is formed but no higher carbonyl-containing compounds are observed. The bridging iodide ligand also appears to limit the site of alkyne attack at $[RhIr(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]$, as it does for $[Ir_2(CO)_2(\mu\text{-}I)(dppm)_2][BF_4]$,[8] to the side of the $MM'P_4$ plane, opposite to the bridging halide group, providing the doubly bridged compound $[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}DMAD)(dppm)_2][BF_4]$ (**4**). The collinear arrangement of CO ligands along the Rh-Ir axis in compound **4** results in long range coupling between the carbonyl carbon atoms of ca. 4-6 Hz.

The reaction of CO with $[RhIr(CO)_2(\mu\text{-}I)(\mu\text{-}DMAD)(dppm)_2][BF_4]$ (**4**) presumably occurs via movement of the iodide ligand out of a bridging position followed by the addition of CO to the coordinatively unsaturated rhodium atom. A rhodium-bound CO ligand then moves into a bridging position. The product, $[RhIrI(CO)_2(\mu\text{-}CO)(\mu\text{-}DMAD)(dppm)_2][BF_4]$ (5), exhibits very strong trans carbon-carbon coupling (47.5 Hz) which has been determined by $^{13}C\{^{1}H\}\{^{31}P\}$ NMR to be due to a trans $OC^{*}\text{-}Ir\text{-}C^{*}O$ interaction. The results of this investigation suggest that the geometry of the mixed-metal complexes $[RhIrCl_2(CO)(\mu\text{-}CO)(\mu\text{-}DMAD)(dppm)_2]$ and $[RhIrCl(CO)_2(\mu\text{-}CO)(\mu\text{-}DMAD)(dppm)_2][ClO_4]$ [3] be re-formulated to conform with the sixteen-electron rhodium, eighteen-electron iridium configuration common to heterobinuclear diphosphine complexes.

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Chapter 7

Conclusions

The work presented in this thesis has focused on binuclear-diphosphine-bridged complexes with the principal goal being the development of the chemistry of dirhodium systems bridged by the bis(dimethylphosphino)methane ligand (dmpm). As noted in Chapter 1 this diphosphine has been much less studied than the diphenylphosphine analogue (dppm). This goal has been achieved through the synthesis of a variety of new "$Rh_2(dmpm)_2$" compounds and investigations of their reactivity in solution. A limited investigation of the related "$RhIrI_2(dppm)_2$" system has also been successful and the results of both studies have helped to illustrate the effect that ligand substitution can have on the reactivity of binuclear-diphosphine complexes.

Throughout the course of this research the well established chemistry of "$Rh_2(dppm)_2$" and "$Ir_2(dppm)_2$" complexes have been used as benchmarks for evaluating the reactivity of "$Rh_2(dmpm)_2$" compounds. In comparing these systems, it has become evident that the greater electron donating ability and smaller steric bulk of the dmpm ligand (relative to dppm) result in electron-rich "$Rh_2(dmpm)_2$" species which tend to coordinate a greater number of π-acid ligands than their "$Rh_2(dppm)_2$" counterparts and appear to undergo much more facile rearrangement than dppm complexes in general. It also appears from these studies that the size of the dmpm ligand more strongly influences the behaviour of these species than does its electron donating ability, by virtue of less steric hindrance to rearrangement and easier access of reagents to the metal centres.

The relatively higher electron density at the metal centres of "$Rh_2(dmpm)_2$" complexes and subsequent greater π-donation from the metal centres to carbonyl ligands is manifested in infrared carbonyl stretching frequencies which are lower than those observed for their direct "$Rh_2(dppm)_2$" analogues. As seen in Chapters 2 and 3, the actual lowering of the carbonyl frequency varies somewhat from a difference of 20 cm^{-1} in the species *trans*-$[RhCl(CO)(dmpm)]_2$ and $[Rh_2(CO)_2(\mu\text{-}Cl)(dmpm)_2][BF_4]$ to 1 cm^{-1} for $[Rh_2(CO)_2(\mu\text{-}S)(dmpm)_2]$ and 13 cm^{-1} for $[Rh_2Cl_2(CO)\text{-}(\mu\text{-}SCNC(S)N(CO_2Et)_2)(dmpm)_2]$. The fact that a carbonyl ligand could not be removed from *trans*-$[RhCl(CO)(dmpm)]_2$ by thermolysis (refluxing toluene, xylenes) or chemical means (Me_3NO), while its dppm analogue readily loses CO under heating in solution is consistent with the generally stronger metal-carbonyl interaction in "$Rh_2(dppm)_2$" compounds.

There is a tendency for the "$Rh_2(dmpm)_2$" species found in this project to coordinate additional π-acid ligands such as CO. As shown in Chapter 2, the resulting chemistry of many of these complexes more closely resembles that of the dppm analogues of iridium than of rhodium. For example, the dicarbonyl complexes $[M_2Cl(CO)_2(\mu\text{-alkyne})\text{-}(diphosphine)_2]^+$ (M= Rh, diphosphine= dmpm; M= Ir, diphosphine= dppm; alkyne= DMAD, HFB) are in contrast with the only observed "$Rh_2(dppm)_2$" species, $[Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-alkyne})(dppm)_2]$ and $[Rh_2Cl_2(\mu\text{-alkyne})(dppm)_2]$.

Since the electron-rich "$Rh_2(dmpm)_2$" system was expected to foster strong metal-carbonyl interactions it was surprising to find that in every case, the additional CO ligands were very readily lost. For the example of $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-}CO)(diphosphine)_2]^+$ it was shown by NMR studies that the dmpm complex actually lost CO more readily than its dppm analogue. The results described in Chapter 4 also show that CO addition to many of the electron-rich Rh(0) and Rh(I) species is reversible simply upon replacing the CO atmosphere with N_2. However, these low-valent species should be even more electron-rich than the Rh(II) compounds of Chapter 2 and therefore have stronger M-CO interactions. It is proposed that the lability of these latter species and "$Rh_2(dmpm)_2$" compounds in general is due to very facile rearrangement within the molecules, a result of the low steric bulk of the dmpm.

Generally, "$Rh_2(dmpm)_2$" compounds are much more fluxional than their closest dppm-bridged rhodium and iridium counterparts. The difference between these systems is most evident from the variable temperature NMR studies of the Rh(0) and Rh(I) species of Chapter 4. The complex $[Rh_2(CO)_3(\mu\text{-}H)(dmpm)_2][BF_4]$ is a prime example, undergoing exchange of all CO's in solution, whereas the dppm species $[Rh_2(CO)_2(\mu\text{-}H)(\mu\text{-}CO)(dppm)_2]^+$ and $[Ir_2(CO)_2(\mu\text{-}H)(\mu\text{-}CO)(dppm)_2]^+$ are not fluxional. Since the labile dmpm species of Chapter 4 also show the greatest deviation in chemical behaviour from that of the dppm systems it appears that the small steric bulk of the dmpm ligand could be more of a contributing factor to the unique chemistry of the "$Rh_2(dmpm)_2$" system than the basicity. Size is certainly an important consideration in the formation of the unusual bis(alkyne) complexes [Rh(CO)(μ-DMAD)-

(dmpm)]$_2$, [$Rh_2(CO)_2$(μ-DMAD)(μ-HFB)$(dmpm)_2$] and [Rh(CO)(μ-HFB)(dmpm)]$_2$, since two alkyne ligands as well as two diphosphine ligands must form bridges between the two metal atoms. The related dppm complexes [$Rh_2(CO)_3(dppm)_2$], [$Ir_2(CO)_3(dppm)_2$] and [$Ir_2(CO)_2$(η^2-μ-DMAD)$(dppm)_2$] show no tendency to react with activated alkyne ligands to provide similar species.

Not surprisingly, the electron-rich "$Rh_2(dmpm)_2$" complexes prepared in this project are much more prone to oxidation than their "$Rh_2(dppm)_2$" counterparts. This is most apparent in the heightened sensitivity of the complexes to air and chlorinated solvents. The greatest sensitivity towards oxidation is observed of the highly electron-rich Rh(0) and Rh(I) complexes of Chapter 4, as represented by [$Rh_2(CO)_3(dmpm)_2$] which rapidly decomposes in air, and reacts with CH_2Cl_2 to yield the dichloride starting material *trans*-[RhCl(CO)(dmpm)]$_2$. In contrast, its direct dppm analogue *trans*-[RhCl(CO)(dppm)]$_2$ can be handled in air and in chlorinated solvents without fear of reaction. Other examples include the complexes [$Rh_2(CO)_2$(μ-DMAD)$(dmpm)_2$] and [$Rh_2(CO)_2$(μ-HFB)$(dmpm)_2$], which also react with CH_2Cl_2 to provide the respective dichloride species [$Rh_2Cl_2(CO)_2$(μ-DMAD)$(dmpm)_2$] and [$Rh_2Cl_2(CO)_2$(μ-HFB)$(dmpm)_2$], and decompose immediately upon contact with air. Although the majority of the compounds prepared in Chapters 2 and 3 are also more sensitive to oxidation than their dppm analogues, several are less so than those of Chapter 4 (a result of their generally higher oxidation state, Rh(I) and Rh(II), and greater coordinative saturation). Thus the compound *trans*-[RhCl(CO)(dmpm)]$_2$ was shown to react with CH_2Cl_2 to yield the tetrachloride species $[RhCl_2(CO)(dmpm)]_2$, but only over an extended period of time.

For the most part, the inherent difficulty of handling the sensitive "$Rh_2(dmpm)_2$" complexes in this project has been overcome by careful manipulation of the compounds under Schlenk conditions and by making the appropriate choice of solvents for the desired reaction. Consequently, it is suggested that the slow growth of dmpm chemistry relative to that of dppm can be attributed not so much to the difficulty in the physical handling of the air-sensitive dmpm ligand or the"$Rh_2(dmpm)_2$" compounds but to the difficulties associated with controlling the reactions with metal substrates and reagents, respectively, and properly characterizing and limiting the subsequent rearrangement of the highly fluxional species which result. For many of the reactions with the reduced species of Chapter 4, the exact reaction conditions were often difficult to determine and slight variations often produced completely different results. Thus it was only after considerable effort that many of the complexes were successfully characterized and prepared in reasonable yield. The preparation of $[Rh_2(CO)_2(F_3CC{=}C(H)CF_3)(dmpm)_2]^+$ from the reaction of $[Rh_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ with H^+ is representative of this problem. For the reaction to proceed, the addition of acid had to be carried out in a nonpolar solvent such as toluene. The same reaction, when carried out in THF, yielded, in addition to a small amount of the vinylic complex, several species which could not be successfully isolated or characterized.

The most significant outcome of this project has been the development of the chemistry of the low-valent, electron-rich compounds of Chapters 4 and 5. In particular, the synthesis of the species $[Rh_2(CO)_3(dmpm)_2]$, $[Rh_2(CO)_2(\mu\text{-DMAD})(dmpm)_2]$ and $[Rh_2(CO)_2(\mu\text{-HFB})(dmpm)_2]$ and the study of their chemistry has led to a variety of unusual vinylic, bis(alkyne), and tris(alkyne) complexes and it is anticipated that further study of these highly reactive compounds will continue to provide insight into the type of reactivity which is possible on binuclear diphosphine-bridged complexes.

Appendix I

Solvents and Drying Agents

Acetone	$CaSO_4$
Acetonitrile	CaH_2
Benzene	Na
Dichloromethane	P_2O_5
Diethyl Ether	Na/benzophenone
Ethanol	Na
Hexane	Na/K
Methanol	Mg turnings
Tetrahydrofuran	Na/benzophenone
Toluene	molecular sieves